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THERMOPLASTIC PREPREG MANUFACTURE BY SOLUTION IMPREGNATION

by

Kendall E. Goodman

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APPROVED:

Alfred C. Loos, Chairman

Kenneth L. Reifsnider

Donald G. Baird

Richey M. Davis

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(ABSTRACT)

Advanced thermoplastic composites are commonly manufactured from "prepreg" materials, where the reinforcing fibers are preimpregnated with resin. The objectives of this investigation were to identify the critical parameters in impregnation of the fiber tow by a thermoplastic solution, and to produce high quality thermoplastic prepreg.

Continuous carbon fibers (AS4 and AU4) were impregnated with a thermoplastic resin solution using a research scale, single tow, drum winding prepreg machine. The parameters varied to control the degree of impregnation of the fiber tow were, weight percent polymer in solution, die size, fiber tow tension, fiber tow velocity, and the use of impregnation pins.

These parameters were varied during the prepregging operation and prepreg samples were evaluated to determine resin content. Viscosity studies were performed on the polymer solutions by means of a Rheometrics Mechanical Spectrometer. Thermogravimetric analyses were performed on the thermoplastic solution and the prepreg. Cross-sectional photomicrographs were obtained to determine the degree of impregnation and the fiber/resin distribution.

Unidirectional laminates were fabricated from the prepreg. Transverse tensile and double cantilivered beam mechanical tests were performed. Fractography photomicrographs were taken. X-Ray photoelectron spectroscopy was used to investigate the possibility of residual solvent in the laminates.

High quality prepreg was manufactured and the critical parameters in the prepregging process were identified and their effect on the prepreg was quantified.

Acknowledgements

The author wishes to thank Dr. Alfred Loos for his guidance and support during the course of this project. The funding for this research was provided by the Virginia Institute for Material Systems, and the National Science Foundation Science and Technology Center; High Performance Polymeric Adhesives and Composites. The author would also like to thank David Leach and Dave Kemmish of ICI for supplying prepreg and polymer that was used in this research. Dr. James Wightman and Steve Wilkinson of the Chemistry Department have been sources of knowledge in the disciplines of polymer chemistry and surface analysis. Dr. Richey Davis and Dr. Donald Baird of the Chemical Engineering Department have provided insight into some aspects of polymer solutions. Dr. Kenneth Reifsnider, Director of the Virginia Institute for Material Systems also provided support and encouragement during the course of this project.

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1.0 Introduction

The use of fiber reinforced composite materials in structural components has increased markedly over the past twenty to twenty five years. The first use of advanced composites in the aerospace industry was the horizontal stabilizer on the F-111 fighter aircraft in 1965 [1].

There are two types of polymers, or matrix materials, which serve to hold the fibers in place and transfer load. The first type is a thermosetting polymer. Fiber reinforced composites with this type of polymer have been thoroughly characterized and have been put to use in many applications. The thermosets chemically react to form an insoluble and infusible network of polymers. After the reaction is complete, the matrix material can be thought of as one giant molecule. Prior to the chemical reaction or cure, these materials must be stored at a sub-ambient temperature to prevent the reaction from progressing. The second class of polymer is thermoplastic. The thermoplastics are long chain molecules which do not undergo any chemical reaction. These polymers can be thought of as strands of spaghetti. When heated, the polymer chains become mobile and the bulk material becomes a viscoelastic fluid.

High performance thermoplastic polymers suitable for use as composite matrix materials have been in existence for a much shorter time than the thermosets. Hence, they are not as well characterized and have not seen as many applications as the thermosets. Some advantages of advanced thermoplastics are:

- much shorter processing time
- ability to be remelted and reprocessed
- can be joined (bonded) without the use of conventional adhesives
- room temperature storage
- some advanced thermoplastic systems have:
  - low water absorption
  - high toughness
  - good solvent resistance

Composite structures can be manufactured from prepreg, which is a thin layer of fibers which have been impregnated with the matrix material. Prepregs have been defined as pre-engineered, ready-to-mold combinations of resin and reinforcement [2]. The first experimental use of prepreg occurred in 1947, followed by the first commercial use in 1948 [2]. Prepreg is available in both woven fiber form as well as continuous fiber, or tape form. Uncured thermosetting prepregs are tacky and have good drape, whereas the thermoplastic prepregs are dry and boardy.

Thermosetting polymers go through a very low viscosity state in the initial stage of curing. The minimum viscosity is on the order of 1.0 Pa-s. The viscosity of thermoplastics in the melt is on the order of 1,000 Pa-s. This high viscosity presents a significant problem in the ability of the matrix material to wet out and impregnate the fibers.

The objectives of this body of work were to identify the critical parameters in impregnation of the fiber tow by a thermoplastic solution, and to produce high quality thermoplastic prepreg. The first step in accomplishing these objectives was to characterize

the viscosity of the polymer solution. The solvent vaporization from the solution and the prepreg was then studied. The effects of the prepregging parameters were analyzed and the tow tension, tow velocity and use of impregnation pins were isolated for further studies. Laminates were manufactured and transverse tensile as well as double cantilivered tests were performed. X-Ray photoelectron spectroscopy was used to search for the presence of residual solvent.

2.0 Literature Review

There are many prepregging techniques which have been utilized in research and production. A description of some of these techniques for prepregging of thermoplastic matrix composites follows. Prepregging can be performed without the use of solvents [3, 4, 5]. The primary problem in this type of prepregging is the high viscosity. One type of solutionless prepregging is film calendering [4, 5], which involves the use of rollers, which apply high pressure to impregnate a polymer film into a collimated fiber arrangement. Another type of solventless prepregging is pultrusion impregnation [6]. This technique takes advantage of the shear thinning nature of some thermoplastic resins. The fiber arrangement is pulled through a die where the impregnation takes place. Powder coating is a prepregging technique which is currently being investigated. In one method, a static charge is applied to the polymer powder which enables it to stick to the fiber tow which is electrically grounded [7]. Subsequently the powder is melted to permanently bond it to the fiber. Another technique involves application of a direct current to the fiber which enables the polymer powder to stick and melt onto the fiber [8]. The solution prepregging technique requires mixing the polymer with a solvent to lower the viscosity, and improve the wettability of the resin onto the fibers. In solution dip prepregging a fiber bundle is passed through a solution bath [3, 4, 5]. The solution

can also be sprayed onto the fibers [3, 4, 5]. Following impregnation, the solvent must be removed by heating the prepreg.

As discussed previously, the solvent is used to lower the viscosity of the resin for prepregging [12]. The solvent must be removed after the prepreg is manufactured; but it is often difficult to remove [13], and there is concern as to whether the solvent may remain at the interface, or elsewhere in the composite. Solvent induced crystallization has been discussed in the literature [14], but was not investigated in this research effort. One problem associated with the use of solvents is that they can induce a molecular weight distribution at the fiber/matrix interface [15]. Because of the solvent, the polymer molecules are much more mobile than in the melt. The polymer mobility allows the low molecular weight species to migrate to the fiber surface, therein creating a molecular weight distribution at the fiber/matrix interface. This low molecular weight interface may degrade the mechanical properties.

Because prepreg is an intermediate material form, there remains some question as to what constitutes a "good" prepreg. Composite properties are often judged by the properties of the fiber and matrix. The composite properties rely heavily on the interphase between the fiber and matrix. Therefore a "good" prepreg should have an optimized interphase, with a homogenous fiber distribution, a homogenous resin content, and should be free of voids.

A fiber volume fraction of 60% is the fiber/matrix proportion used most commonly in carbon fiber reinforced polymer composites. Tensile properties are enhanced with a larger fiber volume fraction, but if the fiber volume fraction is too high, the fracture properties are compromised [9]. Typical fiber volume fractions range from 56 to 65 volume percent fiber [5, 10, 11]. Thermosetting prepregs often have a higher resin content than thermoplastic prepregs. During the curing process, some of the thermosetting resin can be bled off to achieve a fiber volume fraction in the range of 60%. Because of the high viscosity of the thermoplastic resin, there is virtually no resin bleed off during the consolidation process. Hence the fiber volume fraction of the prepreg and the laminate are essentially the same.

3.0 Prepregging Machine Description

The prepregging machine used in this research effort was manufactured by Research Tool Corporation (Model 30). A conceptual diagram of the machine is shown in Figure 1. In Figure 2(a), a photograph of the system is shown. In the background, between the fiber spool stand and the prepregger itself is a plasma treatment unit. The plasma treatment unit can be used to treat the carbon fibers. The fiber spool stand is shown in Figure 2(b). The fiber spool contains a magnetic brake which allows control of the fiber tow tension. The load cell and fiber oven are pictured in Figure 3. The purpose of the fiber oven is to boil off any adsorbed water or other contaminants from the fiber surface [16]. The load cell serves as a continuous monitoring device of fiber tension. It was discovered that the load displayed is twice the actual load on the tow. A free body diagram of the tow as it passes over the load cell rollers is shown in Figure 4; T is the load on the tow and L is the load on the load cell. Static weights were hung from the load cell and the load displayed on the prepregger readout was equal to the weight hung from the cell. Therefore the displayed load is twice the actual load on the tow. The load which is reported in this work is the actual load on the fiber tow, not the displayed load. A diagram of the resin pot is shown in Figure 5. The impregnation bar and the resin pot are shown in Figure 6. The impregnation bar is optional as is the number of pins.

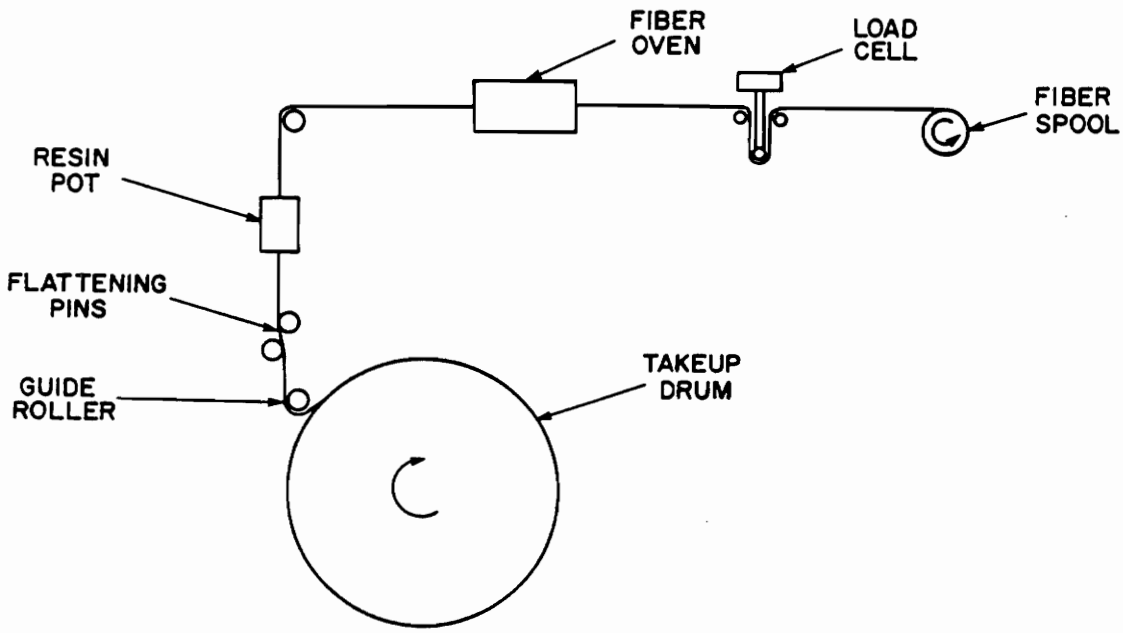
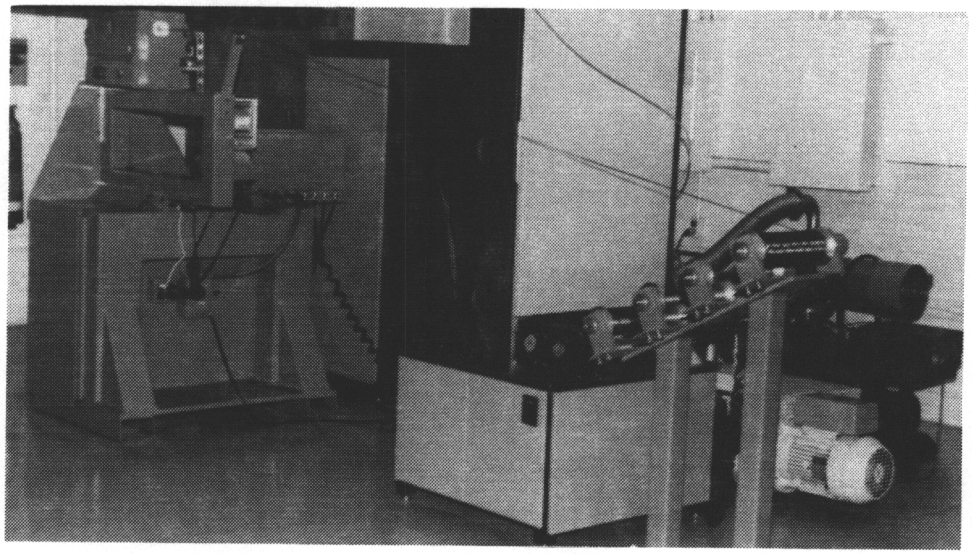
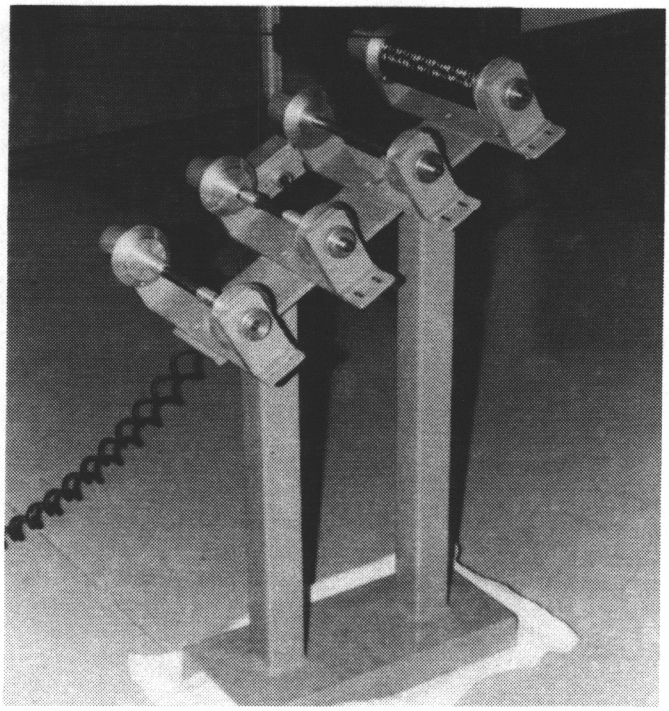


Figure 1. Diagram of prepregging machine.



(a)



(b)

Figure 2. (a) Prepregging machine, (b) Fiber spool stand.

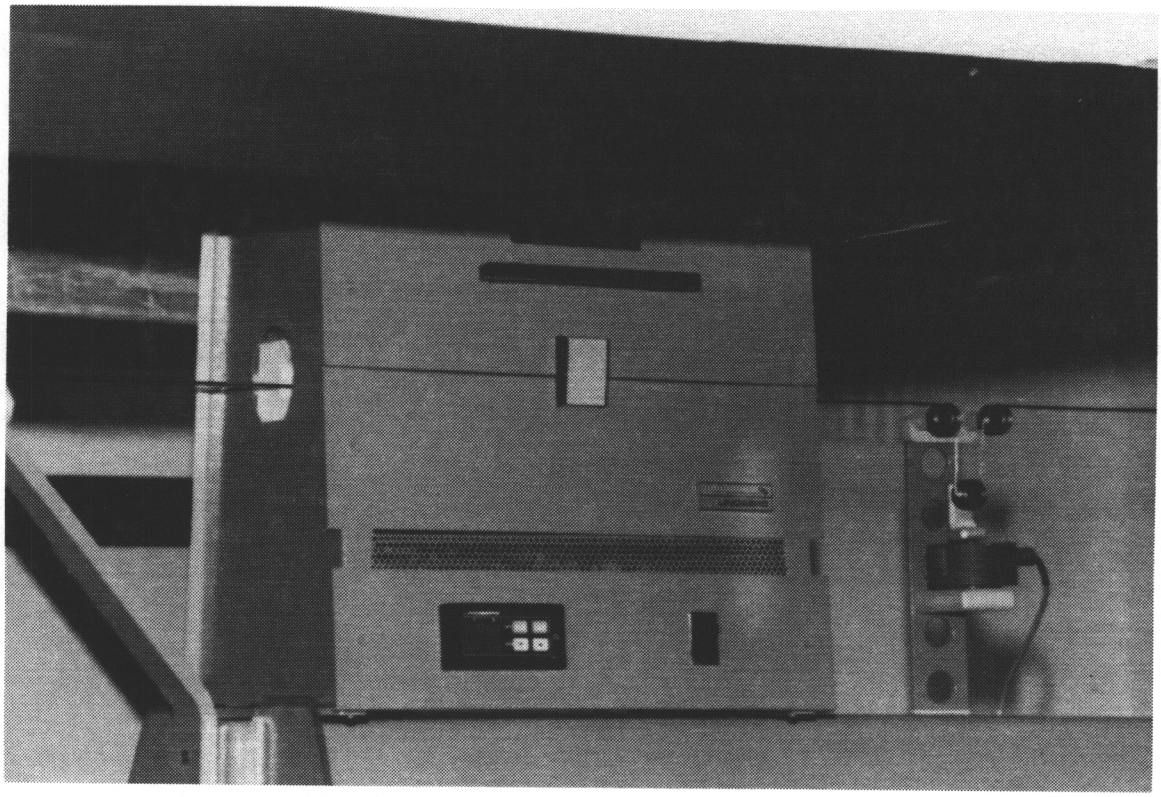


Figure 3. Load cell and fiber oven.

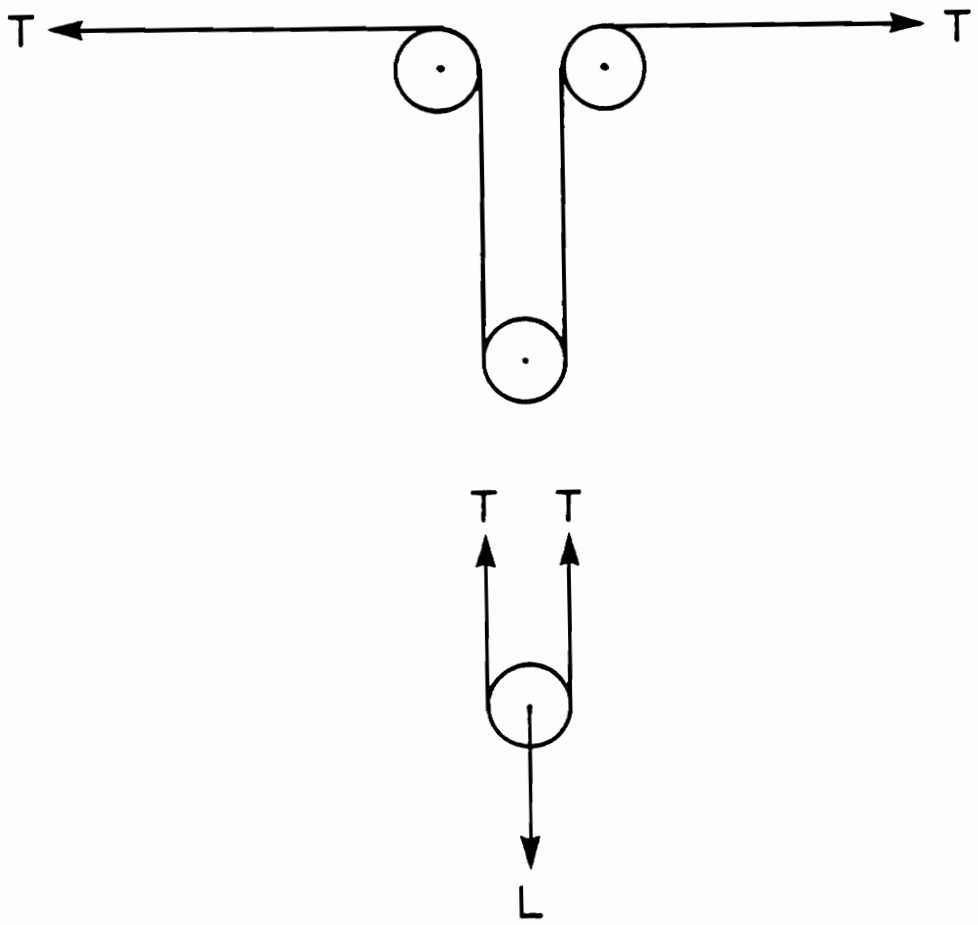


Figure 4. Free body diagram of load cell.

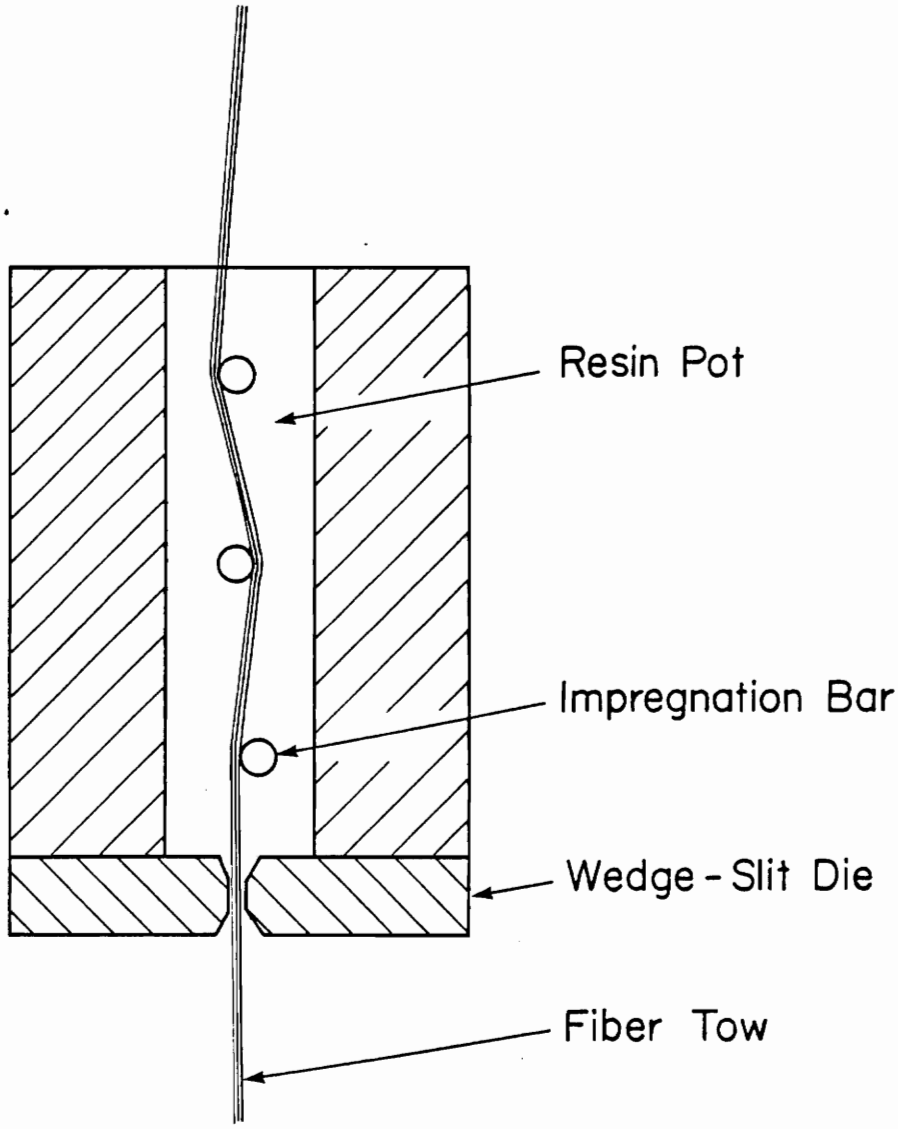


Figure 5. Resin pot.

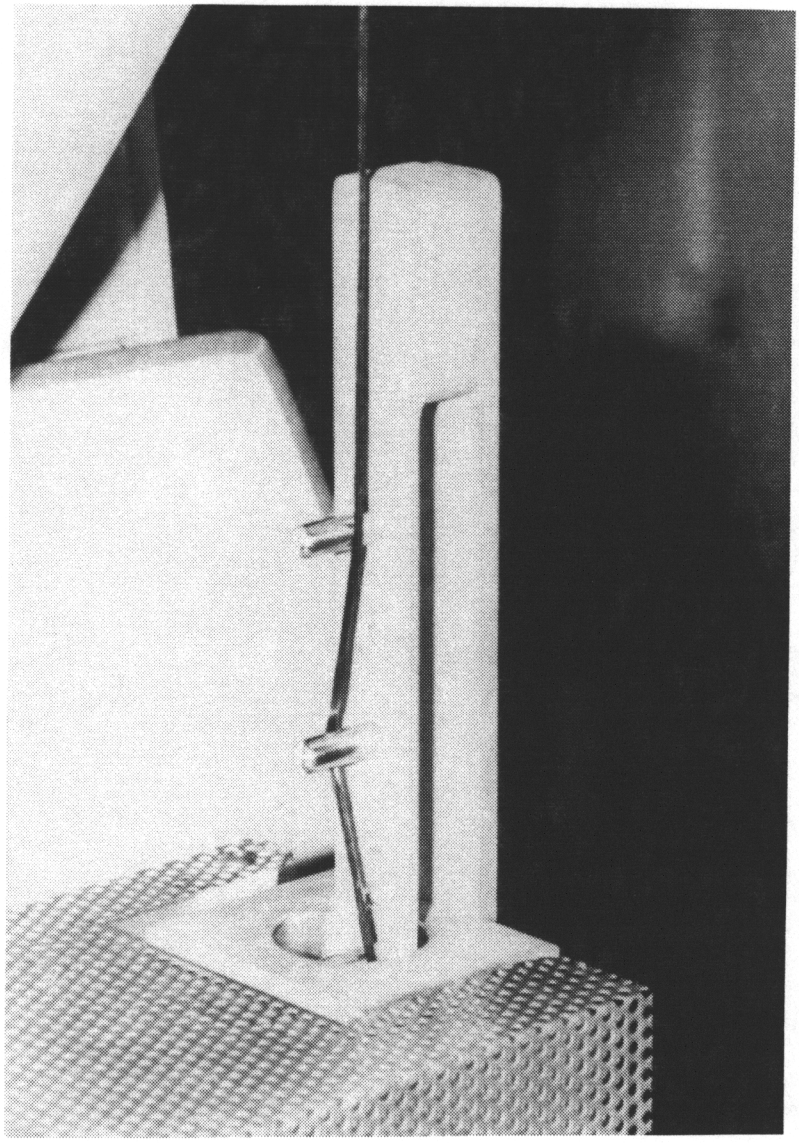


Figure 6. Resin pot and impregnation bar.

The volume of the resin pot is 140 ml and it can be heated to elevated temperatures. The wedge-slit die is shown in Figure 7. The impregnated tow exits the resin pot through the wedge-slit die. The die can be changed to obtain a different die size opening. The resin content of the prepreg can be controlled by changing the die. The flattening pins, which can be heated to elevated temperatures are shown in Figure 8(a). The guide roller, which can be stationary or rolling is shown in Figure 8(b), and is the third and final heated zone. The takeup drum rotates and traverses, and is shown in Figure 9. As the drum rotates and traverses, the tow winds onto the drum and overlaps onto itself to produce a continuous sheet of prepreg. The three heated zones can be controlled from room temperature to 400°C. The drum rotation rate can be varied to produce tow velocities from 0 to 29 cm/s. The drum traverse rate can be varied from 0 to 0.08 cm/s. Up to 44.5 N of tension can be applied to the fiber tow.

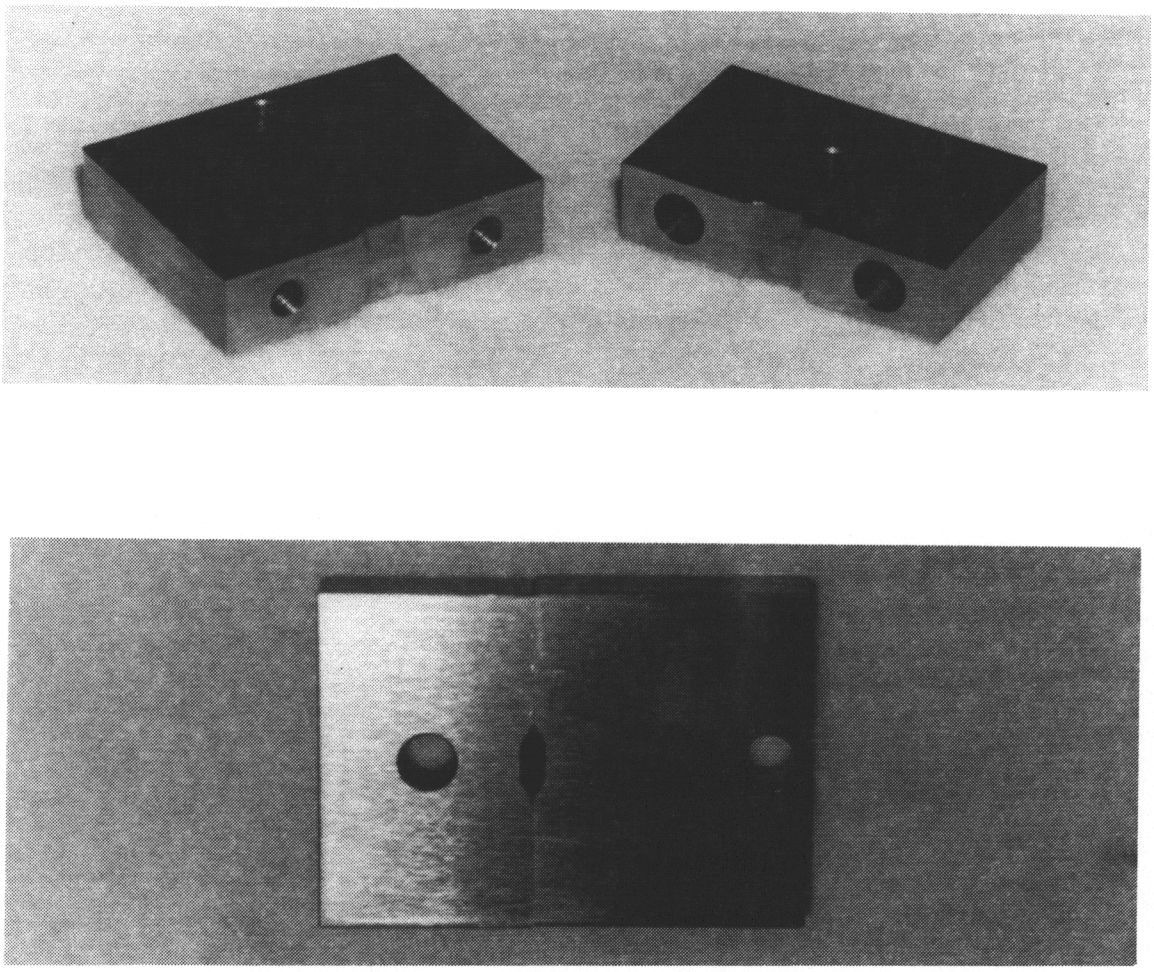
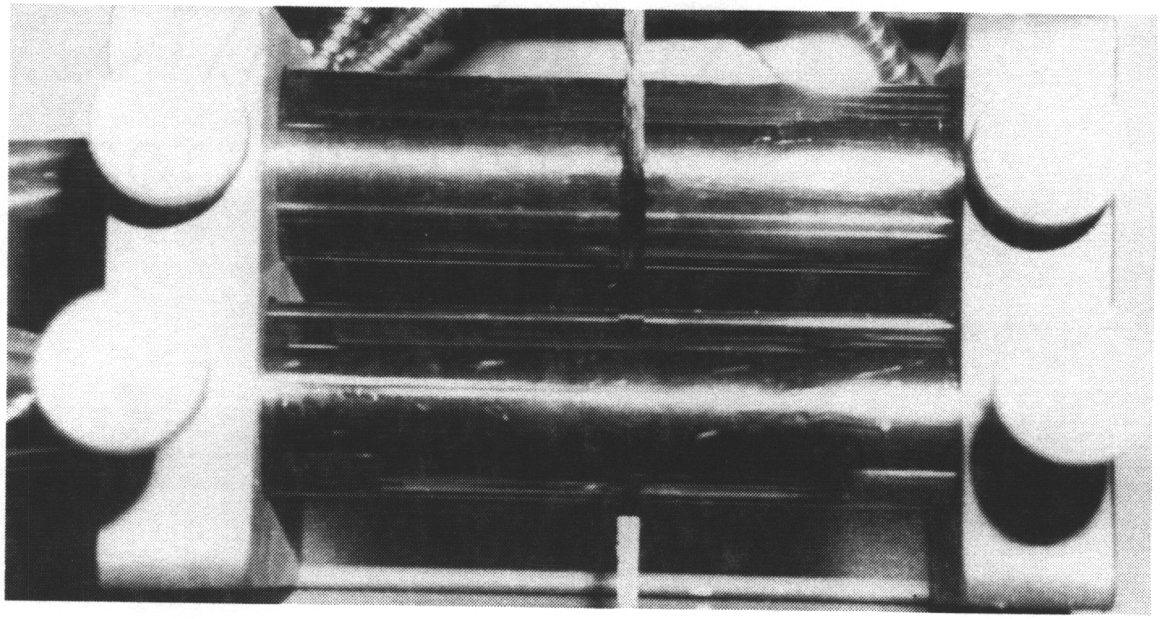
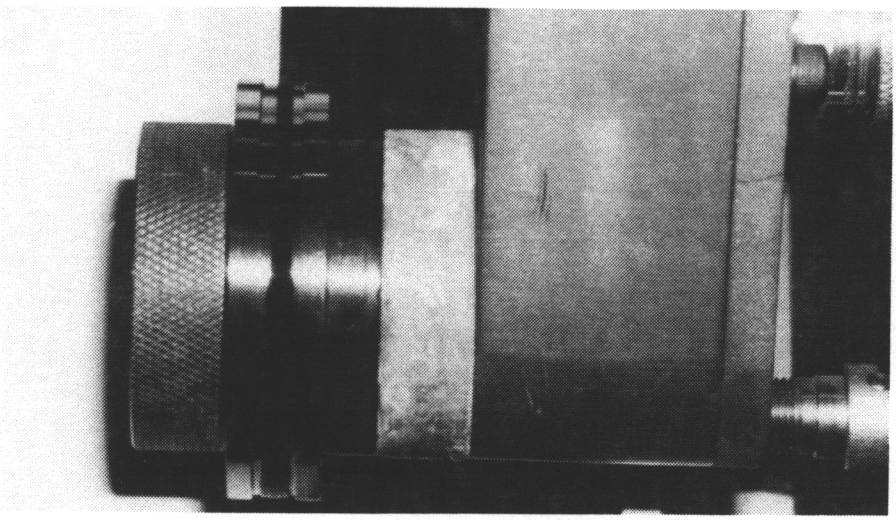


Figure 7. Wedge slit die.



(a)



(b)

Figure 8. (a) Flattening pins, (b) Guide roller.

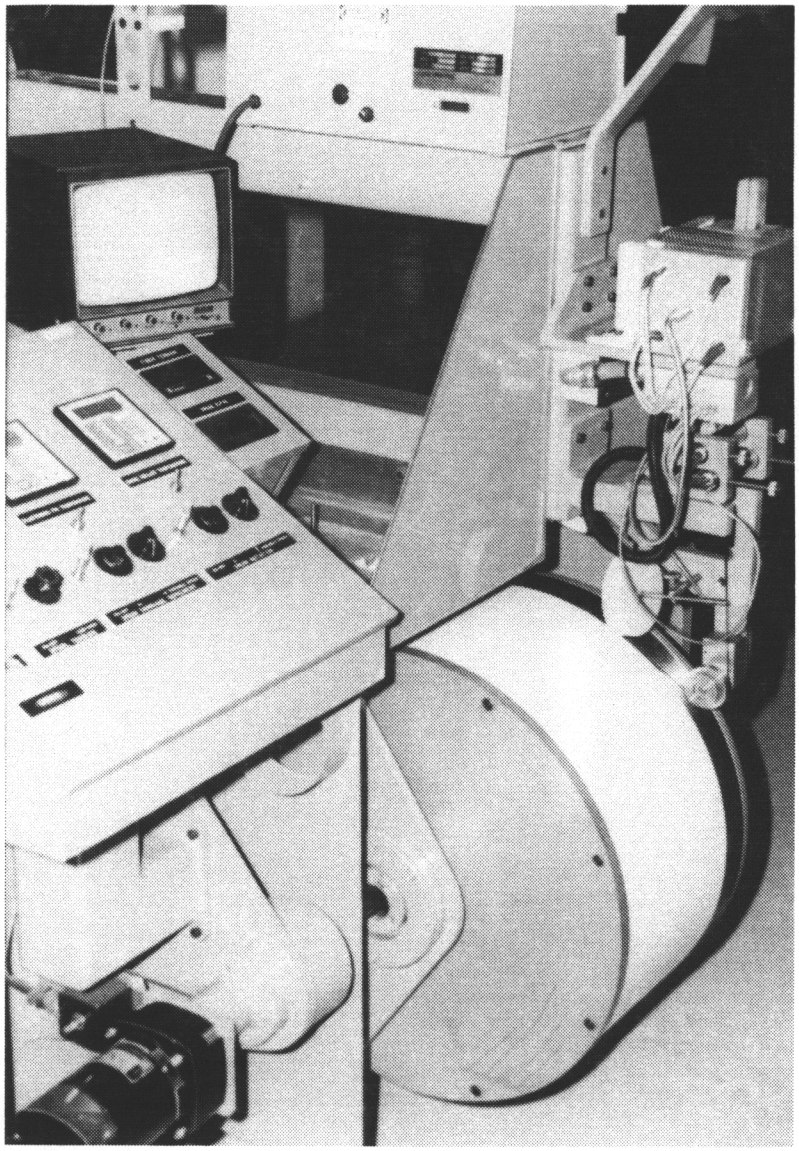


Figure 9. Takeup drum.

4.0 Resin Content Calculation

An effort was made to predict the resin content of the prepreg using simple calculations. The input for the calculations were:

- die size
- fiber yield (g/cm of fiber tow)
- density of polymer
- density of solvent
- density of fiber
- weight percent polymer in solution

The calculations were based on the volume of one meter of prepregged tow. The geometry of this volume is 100 x 0.5588 x 0.0508 cm. The volume consists of the polymer, solvent and fiber. Once the solvent is removed, the volume consists of the polymer and the fiber only. Two assumptions were made. The first was that complete impregnation was achieved (no

voids), and the second was that the impregnated tow had the same cross-sectional area as the die opening. The output of the program was the weight percent polymer of the prepreg, after solvent removal. The variables used in the calculations were:

A	die width (cm)
B	die slit (cm)
L	length of tow (100 cm)
F_y	fiber yield (g/cm)
ρ_p	polymer density (g/cm^3)
ρ_f	fiber density (g/cm^3)
ρ_{sn}	solution density (g/cm^3)
ρ_{st}	solvent density (g/cm^3)
V_t	total volume of 1 meter of impregnated tow including solvent (cm^3)
V_f	volume of fiber (cm^3)
V_{sn}	volume of solution (cm^3)
V_p	volume of polymer (cm^3)
V_{pp}	volume percent polymer in prepreg after solvent removal
R_{sc}	resin solids content (weight percent polymer in solution)
W_p	weight percent polymer in prepreg

The equations used to calculate W_p are as follows:

$$V_t = ABL \tag{4.1}$$

$$V_f = \frac{F_y L}{\rho_f} \tag{4.2}$$

$$V_{sn} = V_t - V_f \tag{4.3}$$

$$\rho_{sn} = \frac{1}{\frac{R_{sc}}{\rho_p} + \frac{1 - R_{sc}}{\rho_{st}}} \tag{4.4}$$

$$V_p = \frac{V_{sn}\,\rho_{sn}\,R_{sc}}{\rho_p} \tag{4.5}$$

$$V_{pp} = 100\left[\frac{V_p}{V_p + V_f}\right] \tag{4.6}$$

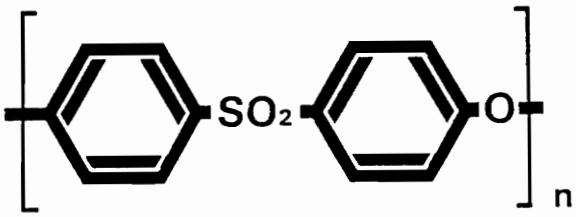
$$W_p = 100\left[\frac{V_p\,\rho_p}{V_p\,\rho_p + V_f\,\rho_f}\right] \tag{4.7}$$

The Fortran source code and sample output are shown in the Appendix.

5.0 Experimental Procedure

5.1 Constituent Materials

The polymer used in this study was ICI Victrex Polyethersulfone (PES), 3600p powder grade. It is an amorphous thermoplastic polymer with a glass transition temperature of 225°C. The chemical structure of PES is:



The solvent was 1-Methyl-2-Pyrrolidinone (a.k.a. N-Methyl-2-Pyrrolidinone, NMP). It is a high boiling solvent with a boiling point of 202°C. A high boiling solvent was chosen so that the solutions would be stable over long periods of time at room temperature. The chemical structure of NMP is $CH_3NCH_2CH_2CH_2CO$.

The two types of polyacrylonitrile (PAN) based carbon fibers used in this study were Hercules AS4-W-12K and AU4-12K. The AS4 fiber is sized and treated, whereas the AU4 fiber is unsized and untreated. A fiber treatment is a chemical functionality put on the surface of the fiber. A fiber sizing is a coating with some thickness. Fibers can be treated, sized, or treated and sized. The purpose of the sizing and treatment is to enhance the mechanical performance of the material system. The AS4 fiber treatment consists of passing the fiber through an electrolytic etching bath after it exits the final processing oven [17]. The fiber sizing is an amine based epoxy which is one micron thick [18]. The fibers supplied were wrapped onto spools in 12,000 (12K) filament tows.

5.2 Solution Mixing

Solutions of 20, 30, 40 and 50 weight percent polymer were prepared. The 40 and 50 weight percent solutions had to be mixed at elevated temperatures because of high viscosity. The mixing is a slow process in which the polymer powder is added to the solvent, that is being stirred by a variable speed laboratory mixer.

5.3 Viscosity Studies

Viscosity studies were performed on a Rheometrics Mechanical Spectrometer RMS-800. Temperature sweeps were run at a constant frequency of 10 radians/second, and a strain of 10%, using the parallel plate configuration. Tests were performed on neat PES, 30, 40, and

50% resin solids content solutions. The viscosity of the 30% resin solids solution was also performed on a Brookfield Cone/Plate Viscometer.

5.4 Prepreg Manufacture

The procedure for manufacturing prepreg was as follows.

1. Attach release paper to the drum
2. Set fiber oven at 250°C
3. Set three temperature zones as desired, or turn off temperature controllers for room temperature prepregging
4. Thread fiber tow through the system, being careful not to twist, and attach tow to the drum
5. Attach die to the resin pot
6. Insert impregnation bar into resin pot (optional)
7. Pour solution into resin pot
8. Start rotation of drum
9. Set drum traverse rate
10. Set tow tension

11. Add solution to resin pot as needed during prepregging, always keeping resin pot near full

5.5 Thermogravimetric Analysis

A Dupont Thermal Analysis System was used to perform the thermogravimetric analysis (TGA) experiments. The Dupont 9900 Computer/Thermal Analyzer and the 951 Thermogravimetric Analyzer Module were used. A two point software temperature calibration was utilized. The two puratonic metals used were indium (157.17°C melt) and lead (327.43°C melt). These two metals were chosen because the testing isothermal temperature of 300°C is between the two calibration points. Nitrogen purge gas was utilized at a flow rate of 60 ml/min. Platinum sample pans held samples of 30 to 100 mg.

5.6 Prepreg Drying

Drying of the prepreg is necessary to remove the solvent. It was first attempted to dry the prepreg under a vacuum bag, but the temperature of drying was too harsh for the bag sealant. Hence, a drying procedure of six hours in a Blue-M forced air convection oven at 300°C was used. The prepreg was placed on steel plates which were treated with release agent.

5.7 Optical Microscopy

Cross-sectional micrographs of prepreg and laminates were taken on a Nikon Epiphot optical microscope. Type 55 Polaroid film was used. The specimens were mounted in Buehler Epoxide mounting material, ground and polished. The different grinding papers were 60, 120, 180, 240, 320, 400 and 600 grit. Nylon polishing cloth was used with 5.0, 1.0, 0.3 and 0.05 micron aluminum oxide powder. A rigid cloth, like thin woven nylon, is preferable. When a softer polishing cloth (felt) was employed, the depth of field between the polymer and the fiber was too great for focusing on the optical microscope.

5.8 Resin Content Tests

The resin content test was used to determine the weight percent polymer in the dry prepreg (solvent removed). The existing ASTM standard tests for resin content determination are not applicable to thermoplastic systems, therefore a new test method was developed. For thermoplastics the type of solvent or acid which will dissolve the polymer is highly dependent on the type of polymer. Since NMP is a good solvent for PES, a solvent extraction technique for determination of resin content of the prepreg was developed with NMP. A Sartorius digital balance with readability of 0.1 mg was used to measure mass. Each replicate consisted of two 2.54 x 2.54 cm pieces of prepreg and there were three replicates for each prepregging condition. The resin content test procedure was as follows:

1. Measure prepreg mass

2. Place each replicate into a beaker with 100 ml of NMP

3. Bring NMP to a boil (202°C) and hold for 30 minutes, stir while boiling

4. Pour out NMP and rinse fibers with fresh NMP

5. Repeat steps 2, 3 and 4 twice (total of 3 times)

6. Rinse with acetone

7. Dry fibers in oven at 220°C for 2 hours (well above 202°C which is boiling point of NMP)

8. Measure fiber mass

5.9 *Laminate Manufacture*

A matched metal die mold was used to manufacture the laminates. A cross-section of the matched metal die is shown if Figure 10. The hot press employed was a Tetrahedron Pneumapress P-400 pneumatic hot press. All laminates were unidirectional. The heat/pressure cycle was as follows:

1. Heat at 6°C/minute to 304°C at a pressure of 689 kPa

2. Apply 3.45 MPa

3. Hold for one hour

4. Reduce pressure to 1.72 MPa

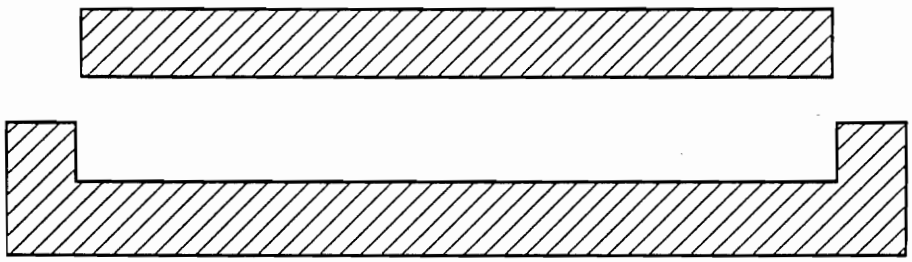


Figure 10. Matched metal die mold.

5. Turn off heat, air passes through platens for slow cool of 1.5°C/minute

An ICI manufactured prepreg consisting of PES/AS4 was used to produce laminates for mechanical tests. This prepreg is not commercially available, but was donated to Virginia Tech for research purposes. A twelve ply, 15.2 x 15.2 cm panel was manufactured with this prepreg for transverse tensile tests. The panel thickness was 0.147 cm, giving a prepreg nominal thickness of 0.0123 cm. A nine ply, 15.2 x 15.2 cm panel of Virginia Tech PES/AU4 prepreg was manufactured for transverse tensile testing. A nine ply panel was chosen to give approximately the same thickness as the 12 ply ICI panel. The panel thickness was 0.156 cm, yielding a prepreg nominal thickness of 0.0174 cm. A second panel of VT PES/AU4 was manufactured for fracture toughness testing. A 2.54 cm kapton film insert was placed at the midplane of the panel on one end. This insert served as a crack initiator. The panel was 12 ply (0.204 cm thick), giving a prepreg nominal thickness of 0.0170 cm. Ultrasonic C-scans were performed on the laminates to check for complete consolidation.

5.10 Laminate Mechanical Tests

5.10.1 Mechanical Test Specimens

The transverse tensile test specimens were cut from the previously mentioned panels. The ends (3.8 cm) of the specimens were tabbed with a standard woven glass/epoxy tabbing material. The specimen width was 2.54 cm, the length was 15.2 cm, the thickness was approximately 0.15 cm and they were cut using a water cooled diamond abrasive saw.

The double cantilevered beam specimens were also cut using a water cooled diamond abrasive saw. The specimen width was 2.54 cm, the length was 15.2 cm, and the thickness

was 0.204 cm. Aluminum blocks were bonded to the same end of the specimen which contained the kapton insert, to allow for insertion of loading pins. The edges of the specimen were painted with water based typewriter correction fluid to allow for good visibility of the crack.

5.10.2 Transverse Tensile Tests

The transverse tensile testing procedure was taken from ASTM D 3039. A servohydraulic MTS load frame with a capacity of 44.5 kN was used, and the crosshead rate was 0.1143 cm/minute. Hydraulic wedge grips with a grip pressure of 5,500 kPa were employed. Five specimens were used from each of the two panels. The specimens were gripped in load control and then the machine was switched to stroke control to avoid application of load during gripping. Strain gauges were mounted in the loading direction, and a Hewlett Packard digital data acquisition system was used. The transverse tensile strength and modulus were calculated.

5.10.3 Double Cantilivered Beam Testing

The MTS load frame and Hewlett Packard data acquisition system were also used in the double cantilivered beam (DCB) testing. A crosshead rate of 0.254 cm/minute and the compliance calibration data reduction technique were utilized [19]. A diagram of the DCB specimen is shown in Figure 11. A total of four specimens were tested. Because of the thinness of the specimen (0.20 cm), care must be taken to use only the data in the linear deflection range of the beam. It has been suggested that only the data in the range:

$$\frac{\Delta}{a} < 0.4 \tag{5.1}$$

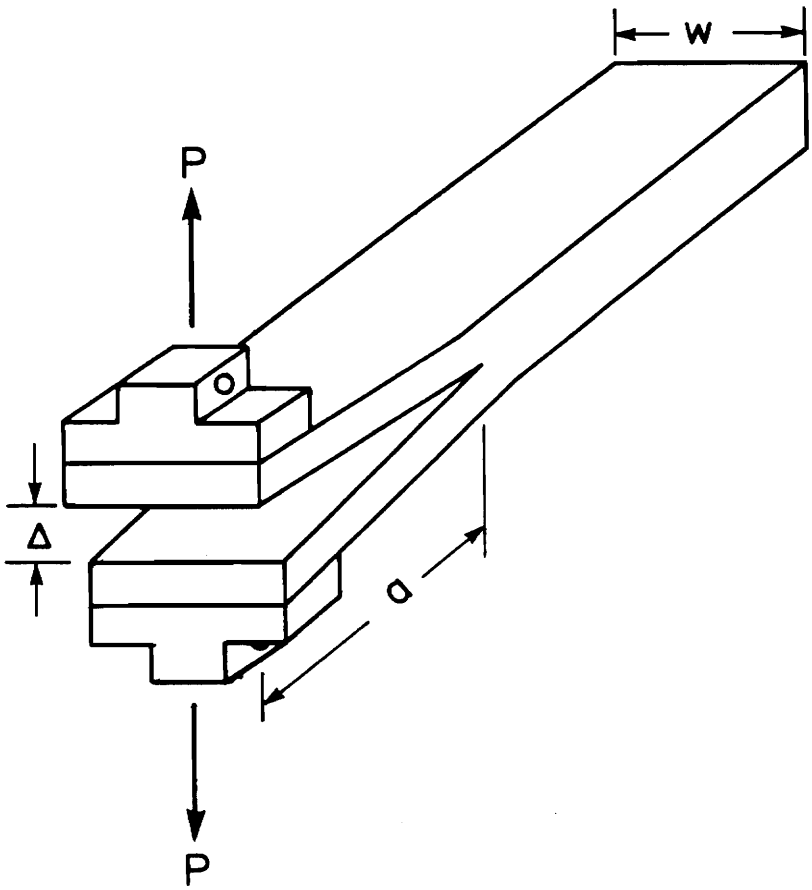


Figure 11. Double cantilivered beam specimen.

is within the linear portion of the beam deflection [20]. As shown in Figure 11, Δ is the crack opening displacement, and a is the crack length. Many who have performed DCB tests [21], use thick specimens (up to 0.53 cm) to avoid nonlinear beam deflection. The DCB testing procedure was as follows:

1. Create natural crack (kapton film leaves blunt crack)
2. Start piston displacement, allow crack to grow 2 to 4 mm
3. Stop piston and hold for 1 minute to allow crack arrest
4. Mark crack on specimen
5. Return crosshead to zero position
6. Measure crack
7. return to step 2
8. Stop test when equation 5.1 is not satisfied

The data reduction for the DCB test begins by calculating the compliance associated with each crack length. The compliance is taken from the loading portion of the curve. A typical load/displacement curve for the DCB test is shown in Figure 12 [22]. After calculating the compliance (c), a third order polynomial is fit to the compliance/crack length data, and a plot of this is shown in Figure 13. If the derivative of compliance with respect to crack length is calculated from the polynomial curve fit, then the mode I critical strain energy release rate of (G_{IC}) can be calculated from:

$$G_{IC} = \frac{P^2}{2w}\frac{\partial c}{\partial a} \tag{5.4}$$

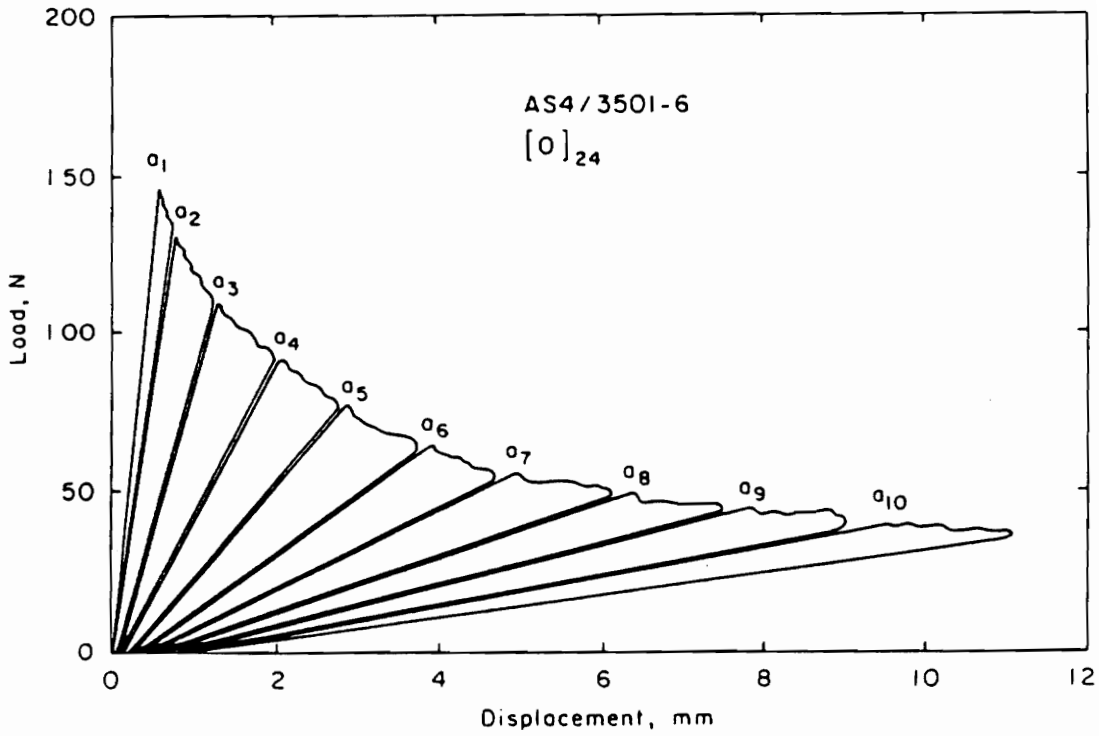


Figure 12. Typical load/displacement curve for DCB test [22].

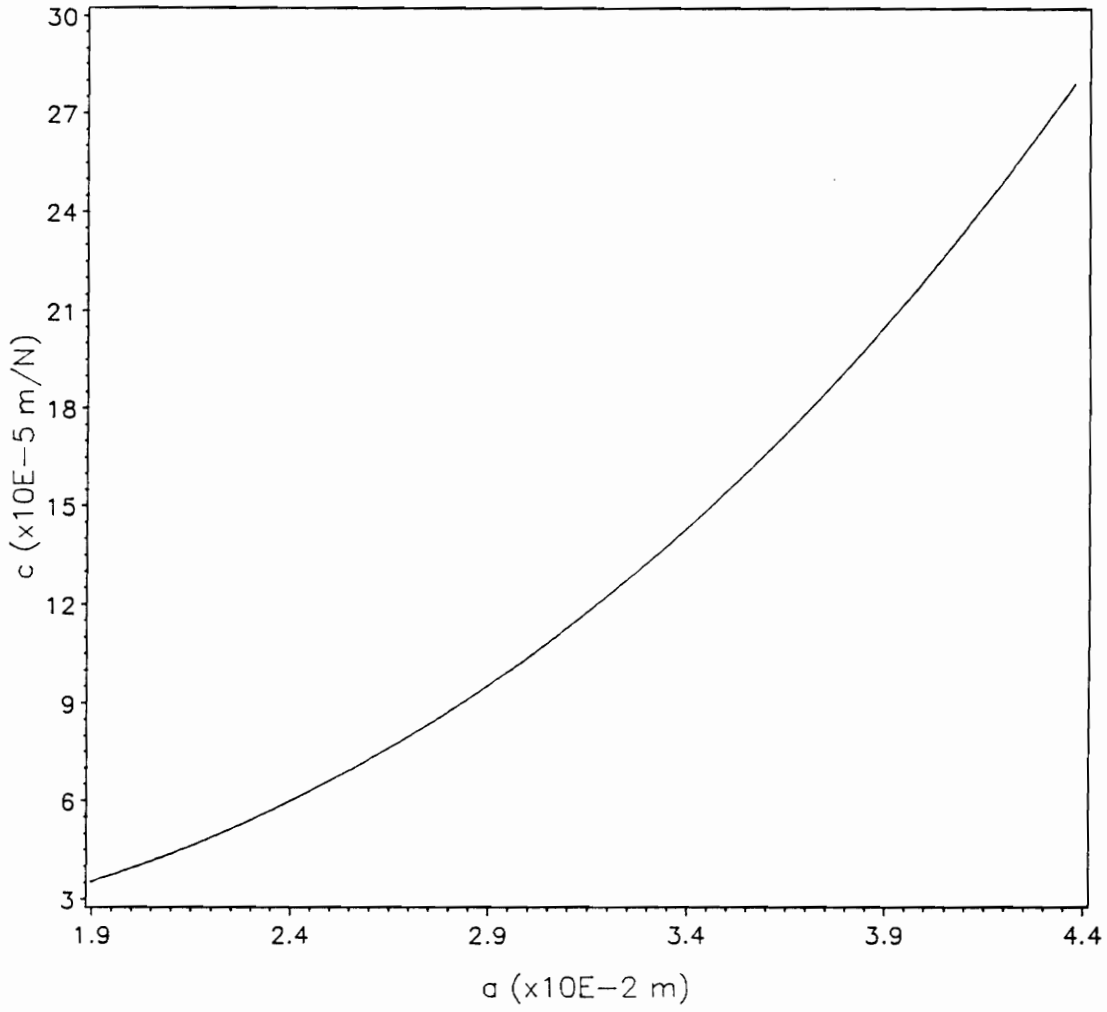


Figure 13. Typical compliance/crack length plot.

Where P is the crack propagation load, w is the specimen width and $\frac{\partial c}{\partial a}$ is the first derivative of the compliance/crack length polynomial.

5.11 Fractography

Fractography was performed on the transverse tensile and double cantilivered beam specimen fracture surfaces. An International Scientific Instruments Inc. SX-40 Scanning Electron Microscope was used. The fracture surfaces were sputter coated with gold prior to investigation.

5.12 X-Ray Spectroscopy

A Perkin Elmer Model 5400 X-Ray Photoelectron Spectrometer (XPS), with a magnesium electron source was used to identify and quantify the atomic species on the surface of the samples. XPS was performed on the DCB fracture surface, polymer powder and the AU4 fiber. The electron beam spot size was 1 x 3.5 mm. A wide angle scan was first performed on each specimen followed by narrow angle scans in the vicinity of each identified element.

6.0 Results and Discussion

6.1 Solution Viscosity

As discussed previously, when prepregging thermoplastics without solvent, elevated temperature and high pressure must be utilized to achieve adequate impregnation of the fibers. The Research Tool prepregger is not capable of high pressure impregnation, therefore a solvent was used to lower the viscosity and to aid wetting of the fibers. The viscosity can be further lowered by the addition of heat. The best prepregging results were obtained from a 30 weight percent polymer solution, impregnated into AU4 fibers at room temperature. The 30% solution was found to have a newtonian flow behavior. The viscosity of the 30% solution was 4.0 Pa-s at a frequency of 10 radians/second and a strain of 10%. It would be inappropriate to claim that 4.0 Pa-s is the optimum viscosity for all fiber/polymer/solvent combinations. The surface energetics between the solution and the fibers may have a significant effect on wetting and impregnation of the fiber tow. Viscosity curves obtained by means of the Rheometrics Mechanical Spectrometer (RMS) for the 40 and 50 weight percent polymer solutions are shown in Figure 14. Even at 190°C the viscosity of the 40% solution is 70 Pa-s, which is considerably higher than the 4.0 Pa-s which gave good results. The 40 weight percent

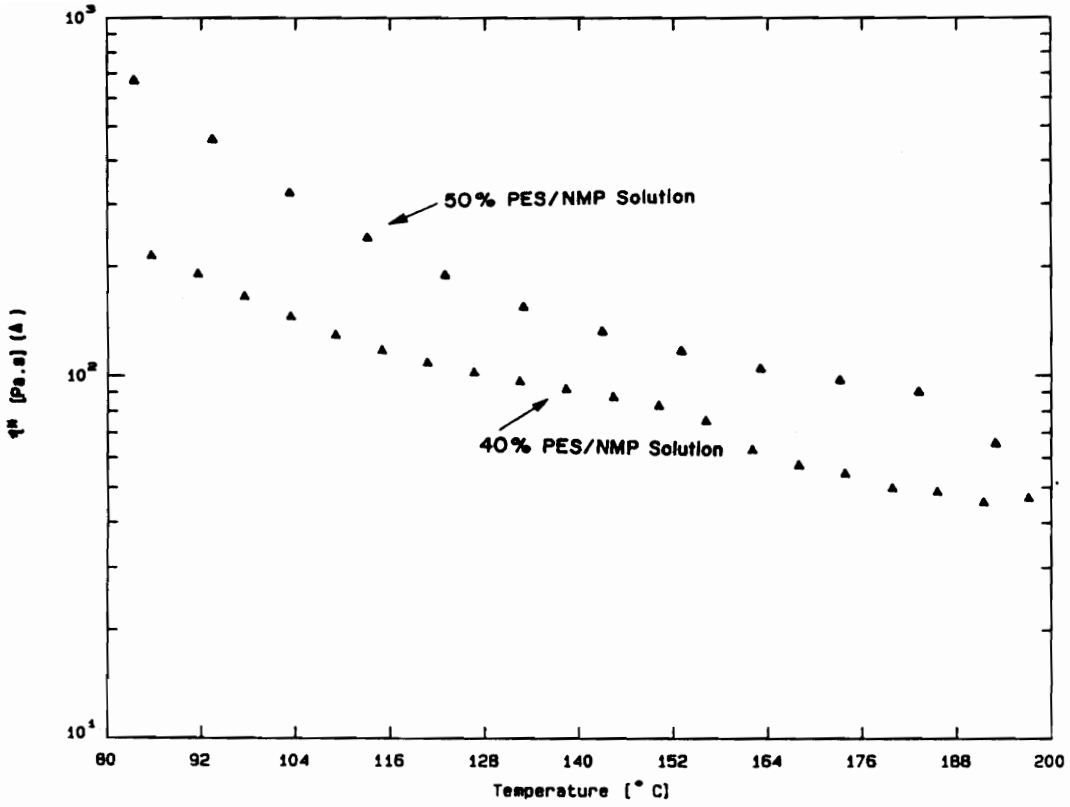


Figure 14. Rheometrics viscosity data for 40 and 50 weight percent polymer solutions, tests performed at a frequency of 10 radians/second and a strain of 10%.

polymer solution viscosity at 200°C is 50 Pa-s, which is also much higher than 4.0 Pa-s. The neat PES (no solvent) viscosity is shown in Figure 15, and this experiment was also performed by means of the RMS.

6.2 Solution Drying

The polymer content of the solution (weight percent), was measured from thermogravimetric analysis (TGA). The weight percent polymer is needed for input into the prepreg resin content calculations. The TGA tests performed on the solution also provide some insight as to the time required to dry the solvent out of the solution. A TGA test performed on a 30 weight percent polymer solution is shown in Figure 16. The temperature cycle is a ramp of 7°C/minute to approximately 300°C, followed by an isotherm at 300°C. This temperature cycle is the same as the cycle used to dry the prepreg in the forced air convection oven. The majority of the solvent evaporates during the first 50 to 60 minutes. After 100 minutes, the solvent has vaporized and the residual polymer is measured to be 28.77% of the original sample weight.

6.3 Prepreg Drying

A TGA test was performed on the wet prepreg (solvent still remaining). This test was conducted in order to observe the time required to dry the solvent out of the prepreg after impregnation. The results are shown in Figure 17. The temperature cycle for the test was designed to be the same as the prepreg drying temperature cycle in the forced air convection

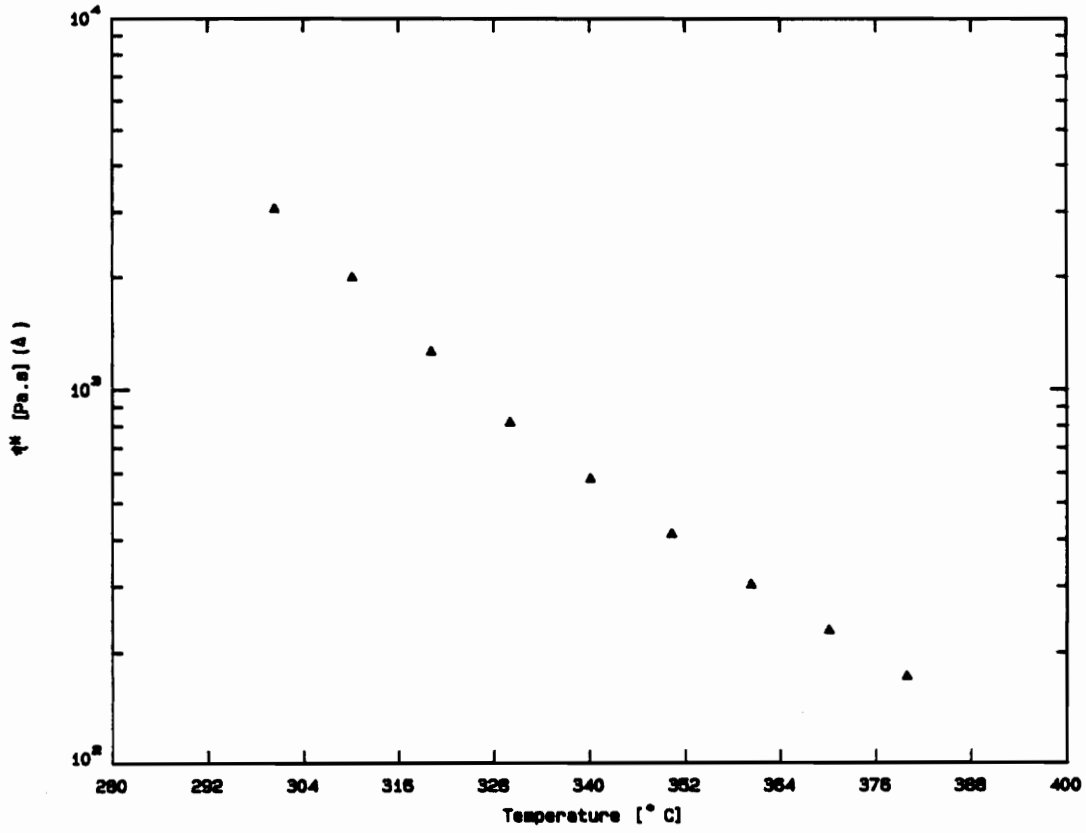


Figure 15. Rheometrics viscosity data for neat PES, test performed at a frequency of 10 radians/second and a strain of 10%.

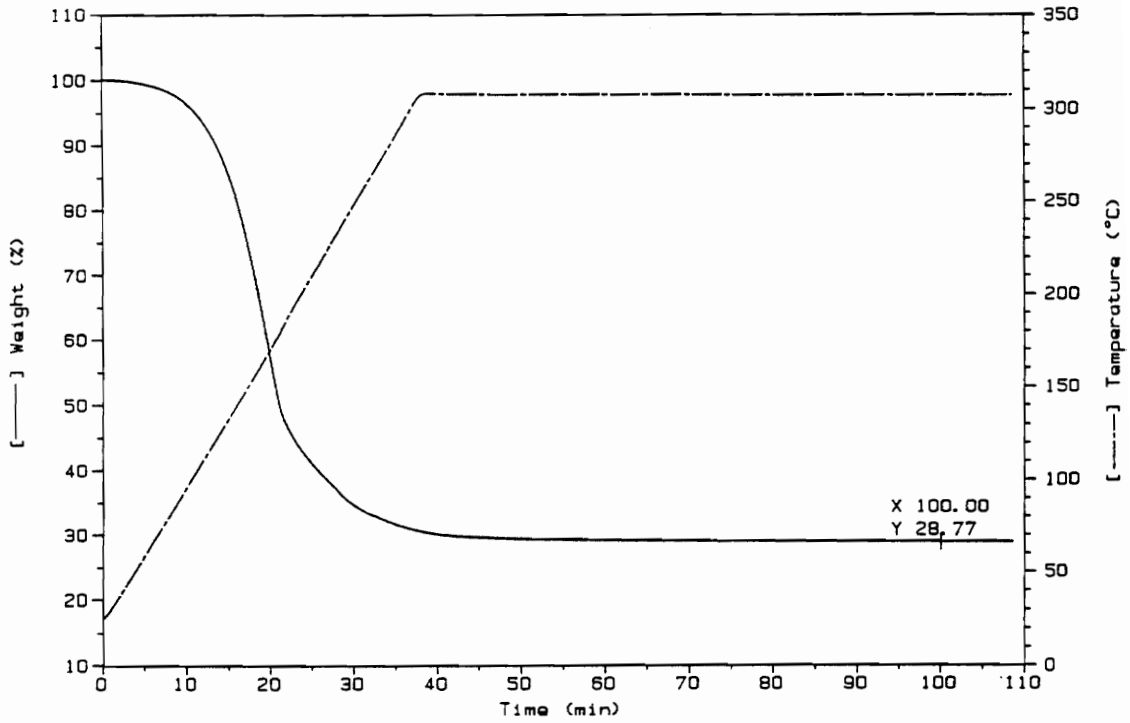


Figure 16. Thermogravimetric analysis of 30 weight percent polymer solution.

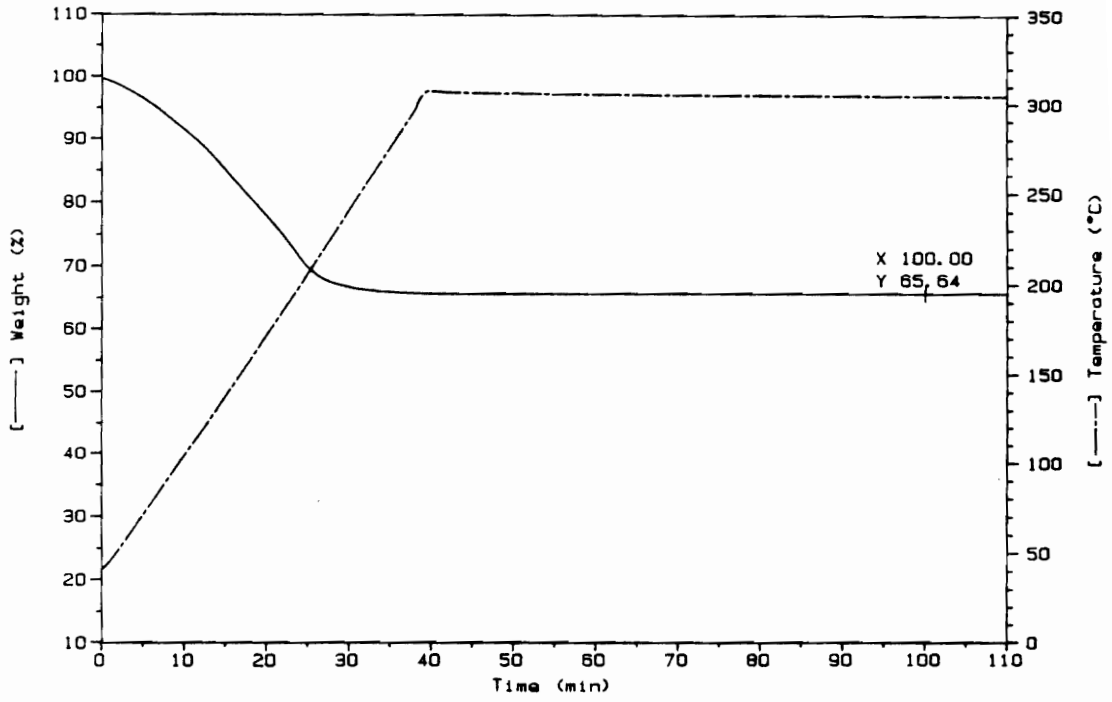


Figure 17. Thermogravimetric analysis of wet prepreg.

oven. It consists of a ramp at 7°C/minute to approximately 300°C followed by an isotherm at 300° C. From the figure it appears that the bulk of the solvent vaporized in the first 30 to 50 minutes of the test. A conservative drying time of six hours at 300°C was decided upon because of concern about the possibility of solvent remaining at the interface or elsewhere in the prepreg.

Application of these elevated temperatures over long periods of time raises concern about polymer degradation. The first TGA test to evaluate polymer degradation was a 1°C/minute ramp of a 30 weight percent polymer solution, and it is shown in Figure 18. The weight loss which appears in the first 300 minutes is due to vaporization of the solvent. The second weight loss which occurs around 400°C is due to polymer degradation. The polymer starts to break up and portions of the molecule will vaporize, hence the observed weight loss. The second TGA test to evaluate polymer degradation was a polymer durability test. The 30 weight percent polymer solution was heated to approximately 300°C and held for 24 hours to see if degradation would occur. The results of this test are shown in Figure 19. The solvent vaporizes in the first 50 minutes and there is no other weight loss, hence there is no polymer degradation. Therefore, the polymer can be subjected to 300°C for a minimum of 24 hours without concern of degradation.

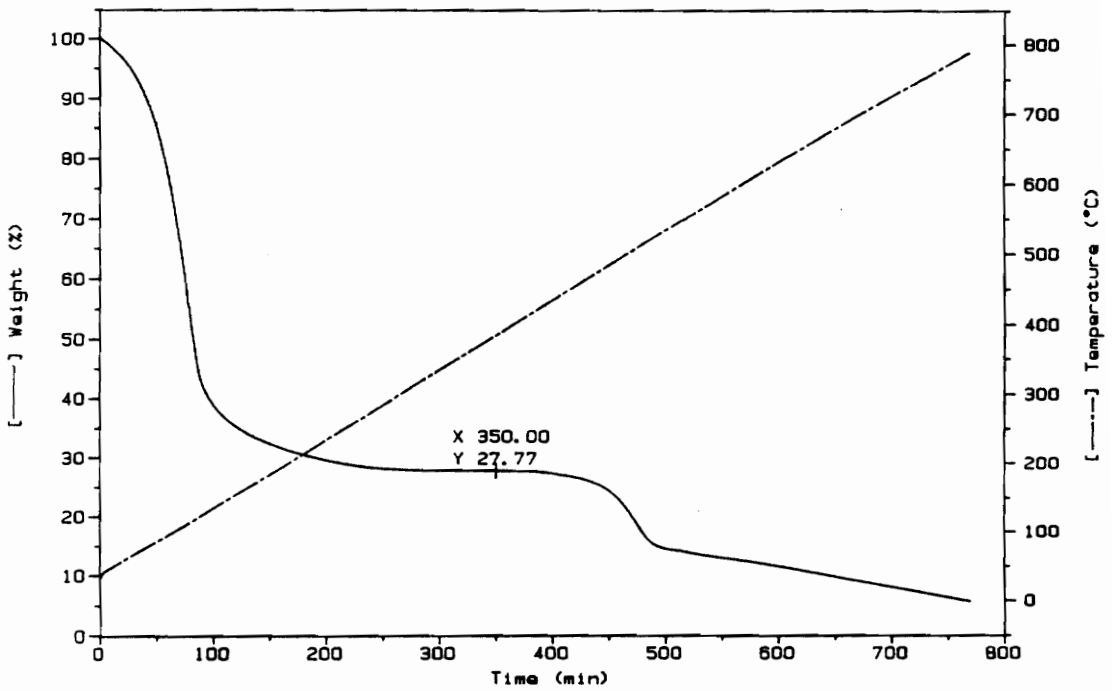


Figure 18. TGA of 30 weight percent solution for polymer degradation.

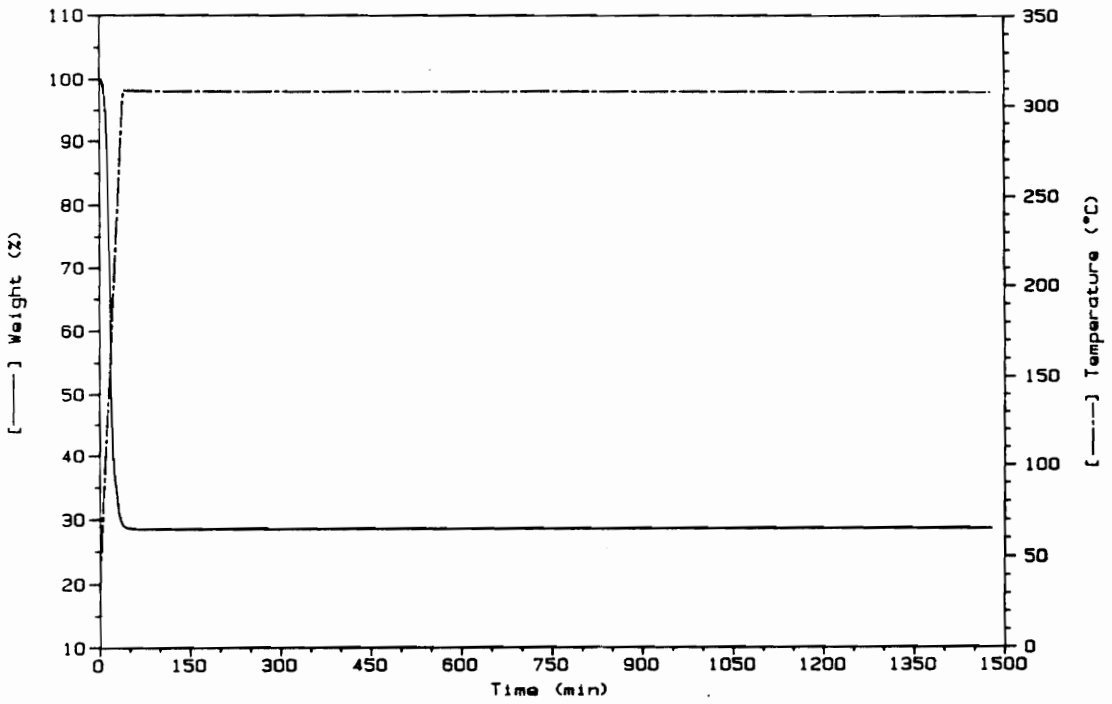


Figure 19. TGA of 30 weight percent solution for polymer durability.

6.4 Prepreg Preliminary Experiments

Preliminary prepregging experiments were performed to identify critical parameters in the prepregging process. Some of the parameters which can be varied in prepregging are:

- weight percent polymer in solution (controls viscosity)
- prepregging temperature (controls viscosity, and amount of solvent vaporization during prepregging)
- fiber treatment
- fiber sizing
- die size
- tow velocity
- tow tension
- number of impregnation pins
- fiber oven temperature

The fiber type used in the preliminary prepregging experiments was Hercules AS4-W-12K. The W designates that the fiber has been sized for winding, and the thickness of the sizing is roughly one micron. The sizing is composed of an amine based epoxy resin [18]. The fiber is treated in an electrolytic etching bath before being sized [17]. There is no curing agent on the fiber surface. The W size is designed to be used with thermosetting systems.

The fiber oven temperature in these experiments was 120°C. For all prepregging experiments the lower flattening pin was in the minimum offset position as shown in Figure 20 (a). A photograph of the flattening pins was shown in Figure 8 (a), Chapter 3. The results of the preliminary prepregging experiments are shown in Table 1. Each column represents one of the prepregging parameters discussed previously, and the last column, titled resulting impregnation, is a qualitative estimate of the degree of impregnation, and the overall integrity of the prepreg. The tow tensions are shown as a range because there was a fluctuation in the tension. This fluctuation could be due to unsteady rotation of the drum, or uneven retarding force from the magnetic brake on the fiber spool. Specimens 1 to 8 were all manufactured from 50 weight percent polymer solution. Most of these specimens were low quality, because the elevated temperatures required to lower the viscosity, also caused the solvent to evaporate from the impregnated tow. Between the time that the tow exited the resin pot and it reached the drum, much of the solvent had evaporated. This caused the tow to become sticky and tend to adhere to the flattening pins and guide roller. Specimens 9 to 13 were manufactured from 30 weight percent polymer solution. The viscosity of the 30% solution is low enough that it can be prepregged at room temperature, which eliminated the problem of solvent vaporization. Also, since the 30% solution had lower viscosity, and contained more solvent, it could impregnate the fiber tow more easily. A recent research program has demonstrated that for lower polymer concentration in solutions, there is a faster wicking rate, or wetting of the fibers [23]. From specimens 9 and 10 it is observed that a lower tow tension is more desirable, and similarly from specimens 11 and 12, a low fiber tow tension gives better results. From inspection of tow velocity in specimens 9 and 11, and specimens 10 and 12, no difference in resulting impregnation can be detected. From specimen 13, the impregnation pins seem to enhance wetting but the pins also cause some fiber breakage due to their small radii.

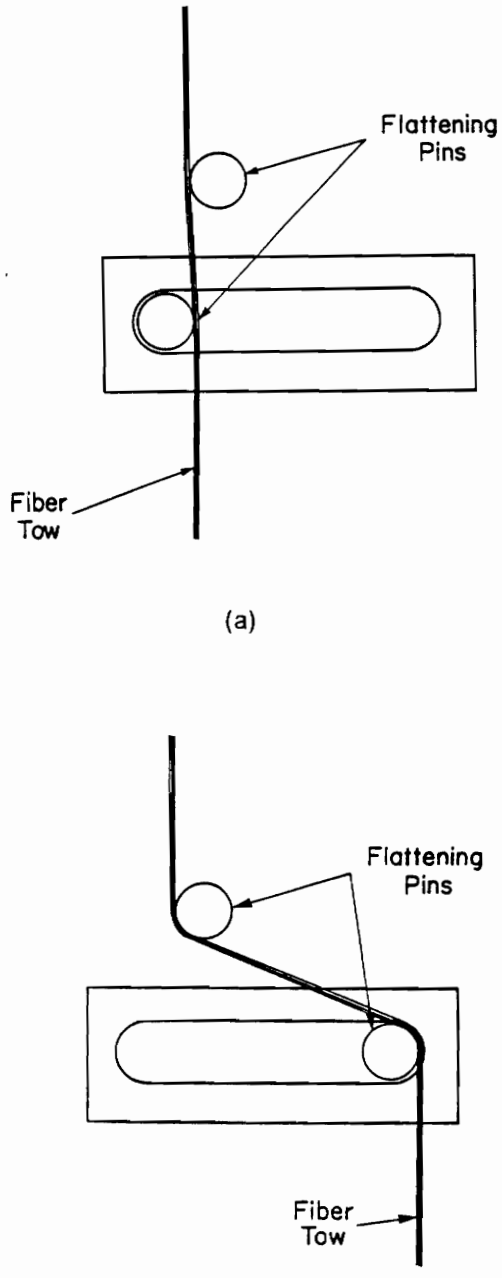


Figure 20. Flattening pins: (a) minimum offset position, (b) maximum offset position.

Table 1. Preliminary prepregging experiments.

SPECIMEN NUMBER	TOW VELOCITY (cm/s)	DIE SIZE (cm)	RESIN SOLIDS CONTENT (% weight)	TOW TENSION (N)	TEMPER-ATURE (°C)	NUMBER OF IMPREG-NATION BAR PINS	RESULTING IMPREG-NATION (1=worst 10=best)
1	28.96	0.559 x 0.0165	50	33.4 - 44.5	99.0	0	1
2	28.96	0.559 x 0.0165	50	0 - 11.1	99.0	0	3
3	28.96	0.559 x 0.0165	50	11.1 - 22.2	99.0	3	5
4	28.96	0.559 x 0.0254	50	33.4 - 44.5	149.0	0	4
5	28.96	0.559 x 0.0254	50	0	149.0	0	4
6	9.65	0.559 x 0.0254	50	33.4 - 44.5	149.0	0	1
7	9.65	0.559 x 0.0254	50	0	149.0	0	3
8	28.96	0.559 x 0.0254	50	33.4 - 44.5	149.0	0	6
9	3.22	0.559 x 0.0254	30	0	22.0	0	8
10	3.22	0.559 x 0.0254	30	33.4 - 44.5	22.0	0	5
11	16.09	0.559 x 0.0254	30	0	22.0	0	8
12	16.09	0.559 x 0.0254	30	33.4 - 44.5	22.0	0	5
13	3.22	0.559 x 0.0254	30	0 - 11.1	22.0	3	8

6.5 Prepreg Resin Content Experiments

Following the preliminary experiments, the decision was made to isolate the tow velocity and tow tension variables for further investigation. The experimental parameters decided upon are shown in Table 2. The tensions shown on the table are measured by the load cell, but in the lower region of the resin pot, the tension will be higher due to the friction of the resin and impregnation pins, if they are used. For all conditions the AS4-W-12K fibers were used, prepregging was performed at room temperature, no impregnation pins were used, the die was 0.559 x 0.0254 cm, and the fiber oven was set at 120°C. After the prepreg was manufactured, it was dried and resin content tests were performed. There were no marked differences in the resin content values of the four specimens, and all gave approximately 10 weight percent polymer. Typical cross-sectional micrographs of these prepregs are shown in Figure 21.

A new test matrix was developed for evaluation of the tow velocity and tow tension. The fiber type was changed to Hercules AU4-12K, which is the same fiber but they are unsized and untreated. This decision was made because of the incompatibility of the epoxy sizing with thermoplastic systems. Also, the unsized and untreated fiber surface serves as a control interface, which future experiments with fiber treatment can be compared to. One problem associated with the unsized and untreated fiber tow is that it is fluffy and wants to come apart unlike the AS4 fiber tow which stays together in a bundle.

In the original prepregger arrangement, the fiber passed through the load cell before it reached the fiber oven. The positions of the fiber oven and load cell were switched so the fiber oven could be as close as possible to the resin pot. The smaller distance between the resin pot and the fiber oven, make it less likely for the contaminants to readsorb onto the fiber surface between the oven and the resin pot. The fiber oven temperature was increased to 250°C. A larger die (0.559 x 0.0508 cm) was used because of the low resin content of the previous prepregs. The prepreg was manufactured from 30 weight percent polymer solution at room temperature. The results of these experiments are shown in Table 3. The numbers

Table 2. Prepregging experiment test matrix.

		TOW TENSION (N)	
		0 - 11.1	11.1 - 22.2
TOW VELOCITY (cm/s)	1.61	#1	
	9.65	#2	#3
	16.09	#4	

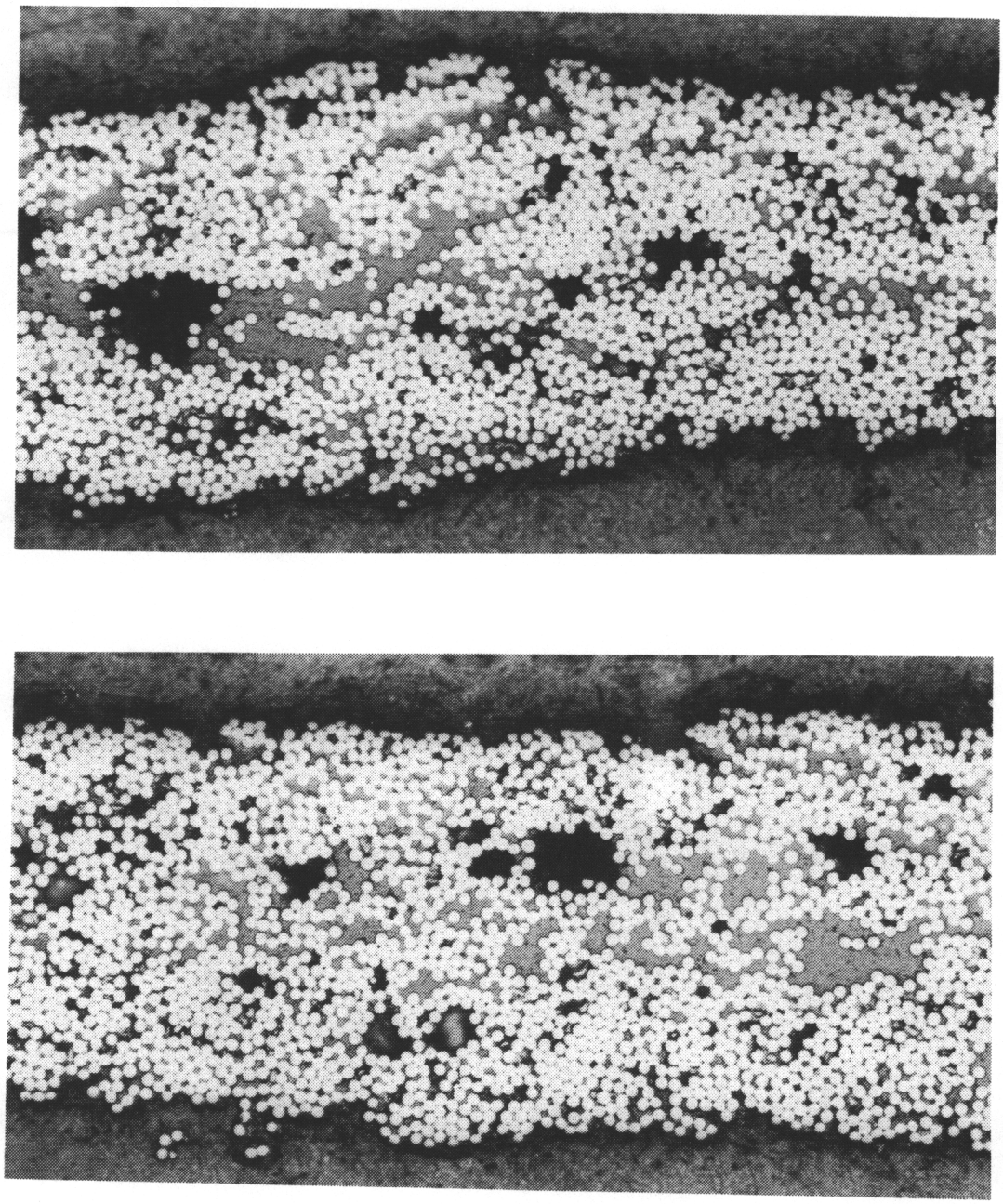


Figure 21. Typical cross-sectional micrographs of prepreg (240X).

Table 3. Prepregging resin content results.

		TOW TENSION (N)		
		0 - 11.1	11.1 - 22.2	33.4 - 44.5
TOW VELOCITY (cm/s)	1.61		#1 29.7	
	9.65	#2 29.9	#3 32.1 *	#4 33.8
	29.0		#5 33.9	

* #6, same as condition #3, but with 3 impregnation pins 37.1

in the table are the prepreg resin content (weight percent polymer, #1 and other numbers designate the prepregging condition) and the results in the table are for prepregs made without impregnation pins. The resin content increases with:

- increased tow velocity
- increased tow tension
- use of impregnation pins

The effect of tow velocity on the resin content may be due to the pressure that develops within the wedge slit die. A fluid flow model has been generated for the wedge slit die geometry [24]. This flow model illustrates the sharp increase in pressure near the land region of the die, and demonstrates that this pressure increases, with an increase in tow velocity. The high pressure region due to the wedge-slit die is illustrated in Figure 22.

The improved impregnation due to higher tow tension may be caused by increased capillarity and wicking forces, which cause impregnation of the polymer solution into the fiber tow. The equation for liquid rise into a capillary tube is:

$$\Delta p = \frac{2\gamma}{a} \cos\theta \tag{6.1}$$

Where Δp is the pressure difference between the top and bottom of the liquid in the capillary tube, γ is the surface tension of the liquid, a is the radius of the capillary tube, and θ is the contact angle between the liquid and the capillary tube. For smaller capillaries (a), the equation shows that the pressure difference (Δp), will be greater. The spacing between the carbon fibers can be thought of as a capillary. The increased tow tension tends to bring the fibers closer together, therefore the increase in capillary forces may be causing the improved impregnation.

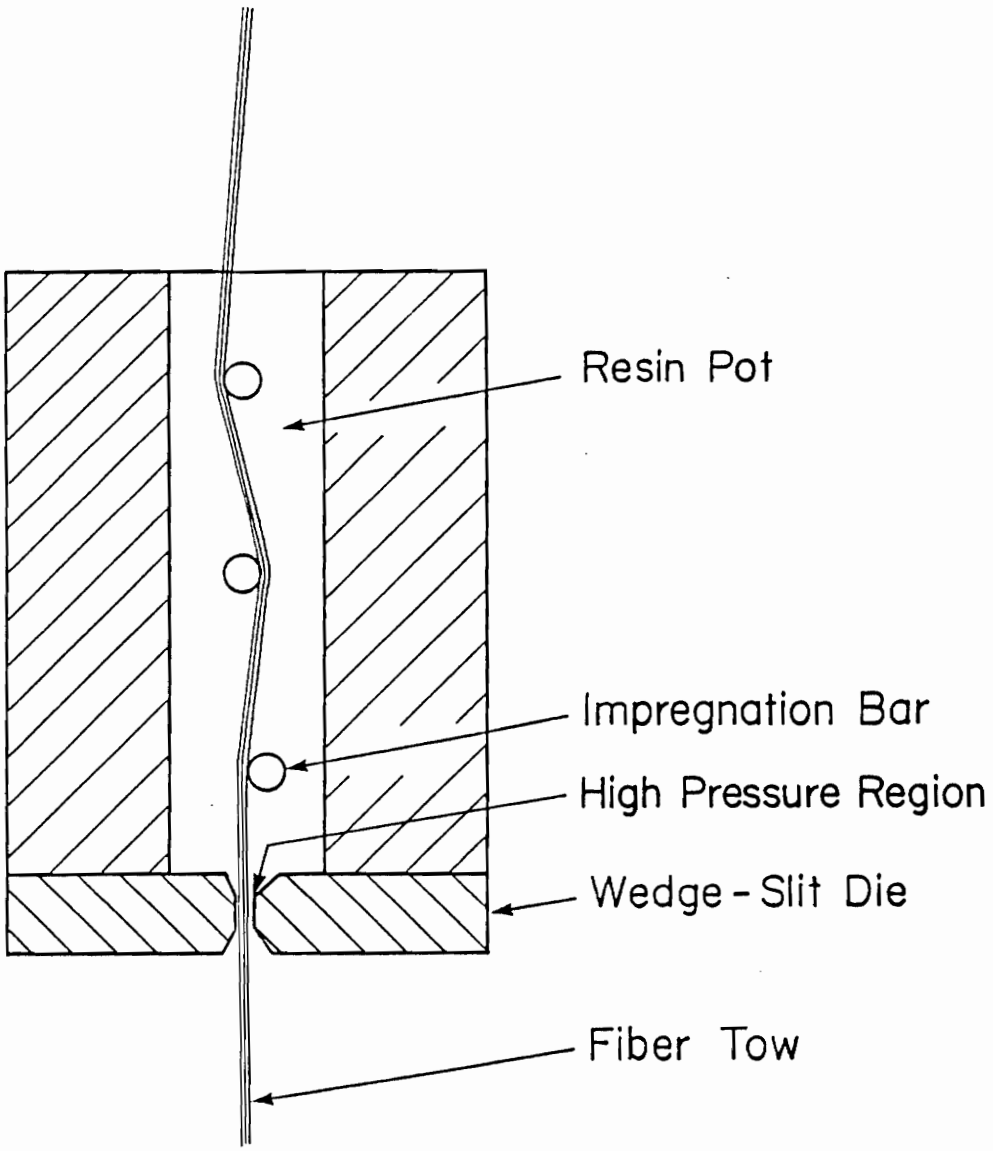


Figure 22. High pressure region due to wedge-slit die.

The increase in tow tension may also act to hold the fibers in a rigid arrangement, preventing them from collapsing into a tight bundle as they pass through the wedge-slit die. Because the tow doesn't deform into a tight bundle, it is more permeable and hence more easily impregnated.

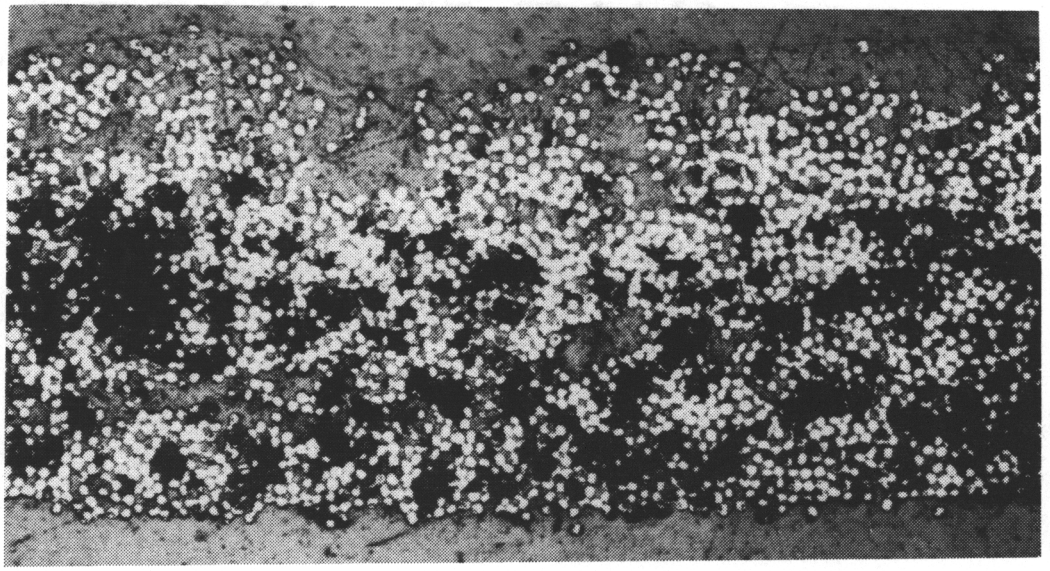
In previous experiments the lower fiber tow tension appeared to give better wetting, but the previous results were for AS4 fibers and the evaluation was qualitative.

An experiment was performed to determine the effect of the type of fiber (AU4 or AS4), on impregnation. The prepregging conditions were the same as condition #6 (best prepreg) on Table 3. The resulting micrographs are shown in Figure 23. In Figure 23 (a), the AS4 prepreg is shown and in Figure 23 (b) the AU4 prepreg is shown. The inadequate impregnation of the AS4 fibers may be due to the surface energetics between the fibers and the solution. The unsized fibers spread out on the impregnation pins more easily than the sized fibers, therefore the poor impregnation of the AS4 fibers may also be due to the restricted spreading of the sized tow as it passes over the impregnation pins.

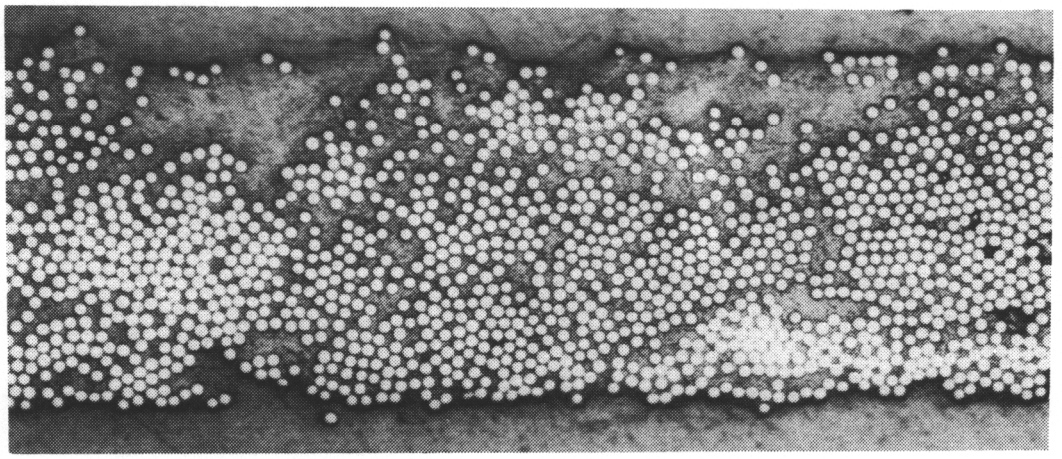
The impregnation pins may cause better wetting due to the elevated pressure caused by the resin trapped between the fiber tow and the impregnation pin. There are three high pressure regions due to the impregnation pins, and one is pointed out in Figure 24. As previously mentioned, the pins also cause a small amount of fiber breakage.

After the prepregged tows were wrapped onto the drum the polymer solution flowed to the surface of the prepreg, similar to fiber compaction which has been observed in filament winding [26]. Cross-sectional micrographs of prepregging condition #6 from Table 3, are shown in Figure 25; (a) illustrates the complete wetting of the fiber tow, and (b) shows a void in the region where the fiber tows overlap onto the drum. This void is most likely caused from entrapped air when the tow was wound onto the drum and overlapped on the previously wound portion of the tow. The resin rich surface of the prepreg can be observed from this figure.

In Figure 26 (a), condition #2 from Table 3 is shown. In Figure 26 (b), condition #1 from Table 3 is shown. Micrographs of commercially produced prepreg are shown in Figure 27.



(a)



(b)

Figure 23. Prepreg micrographs (240X): (a) PES/AS4, (b) PES/AU4.

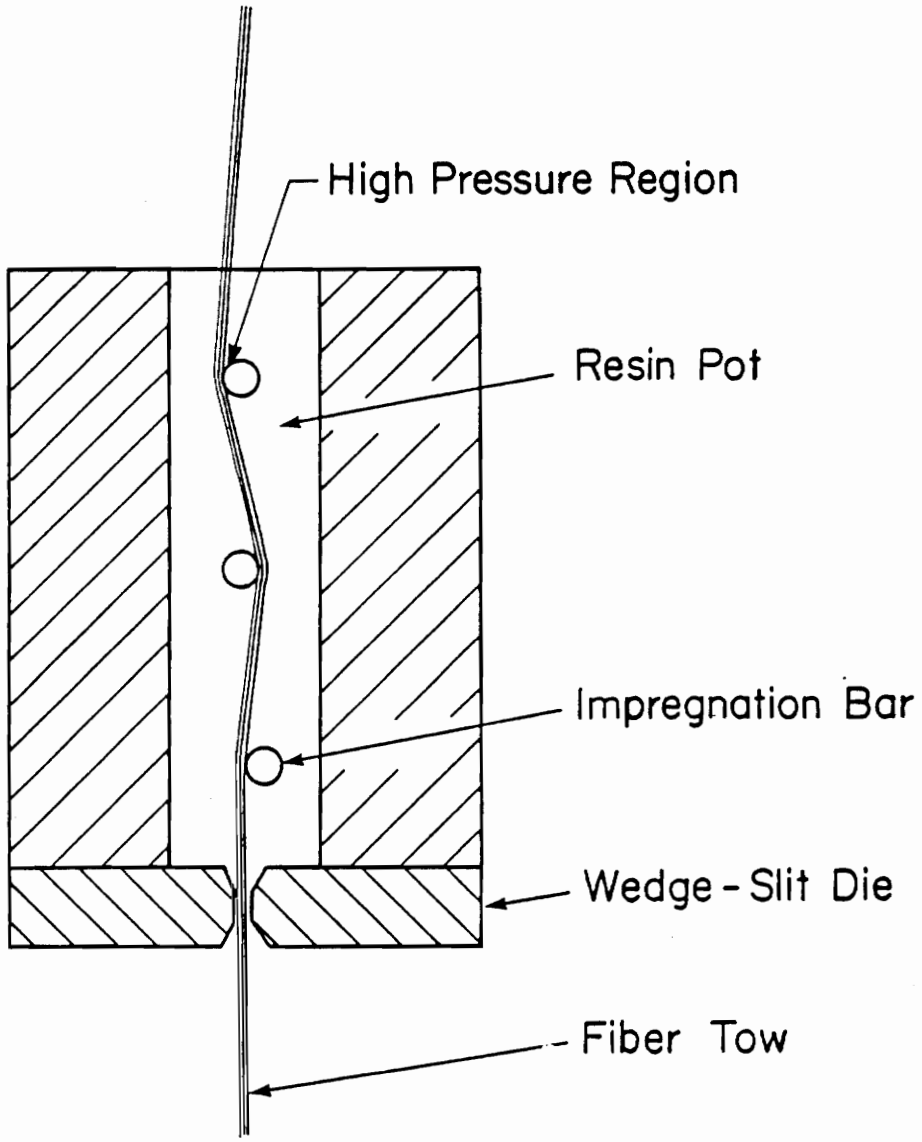
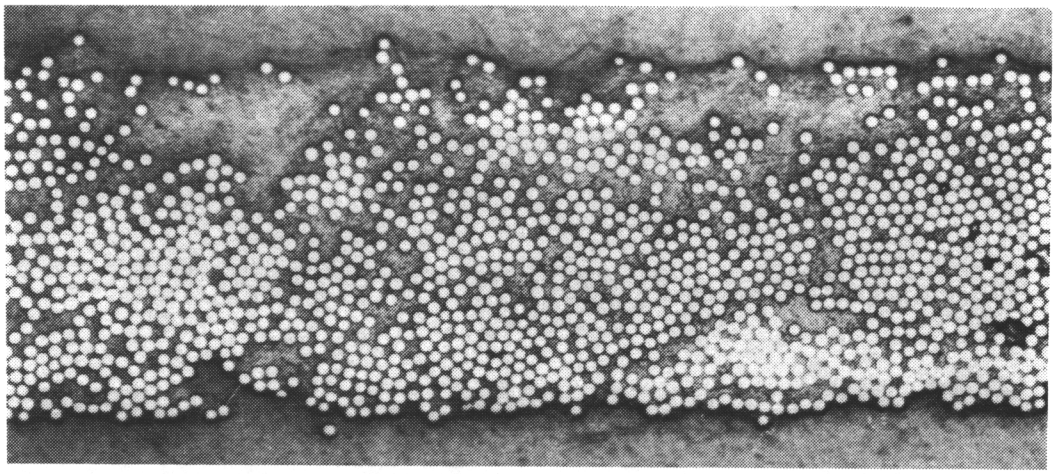
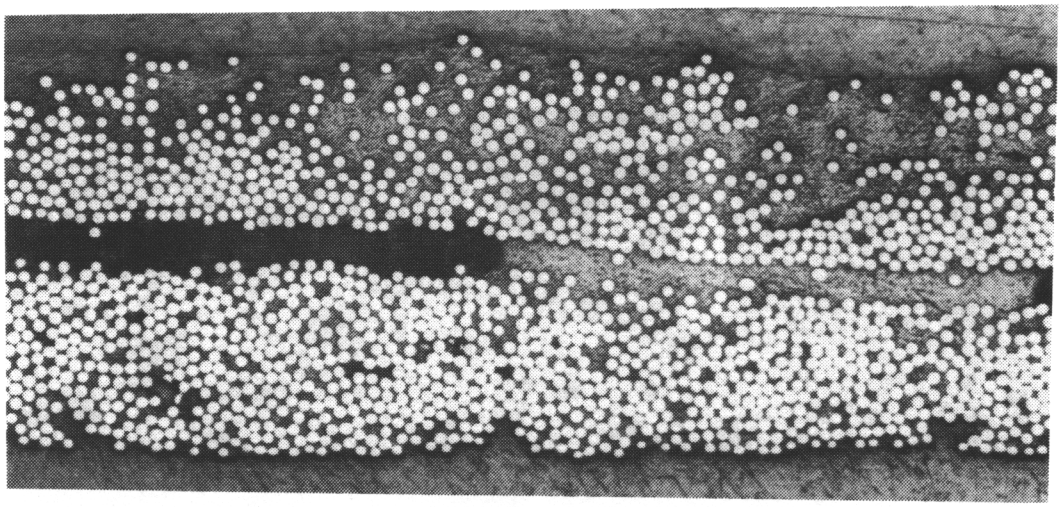


Figure 24. High pressure regions due to impregnation pins.

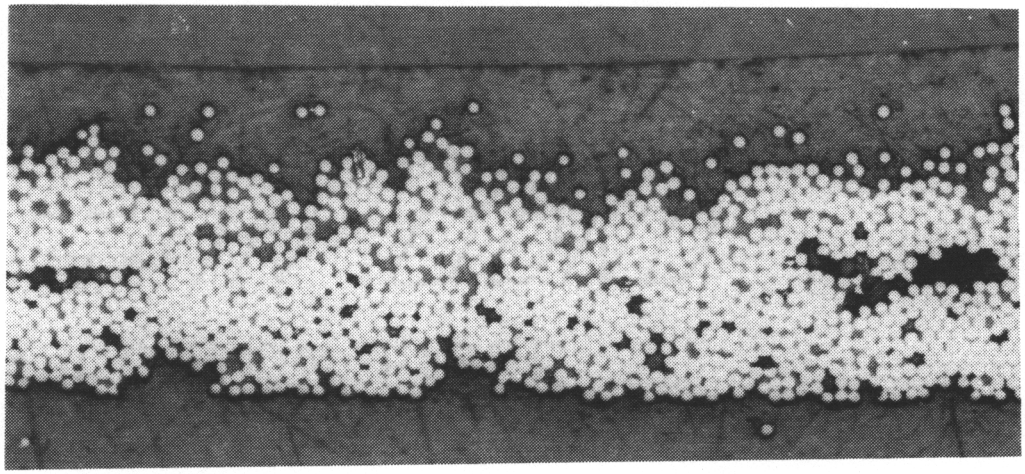


(a)

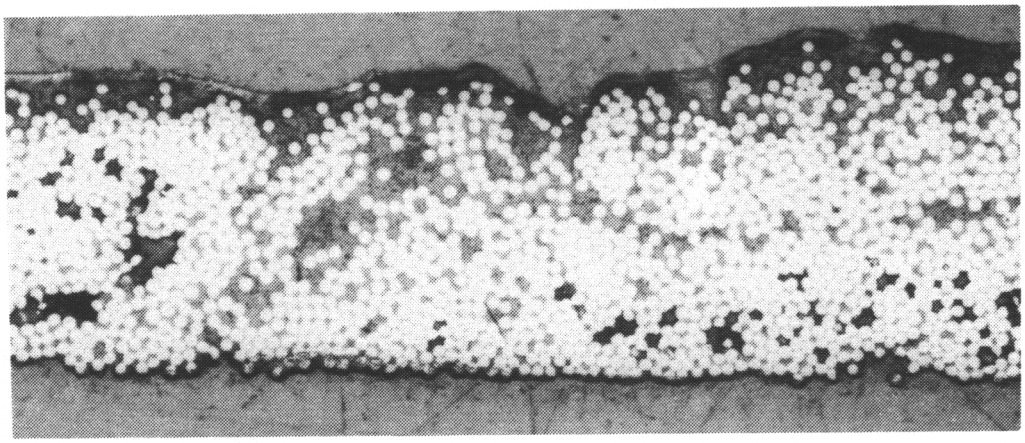


(b)

Figure 25. Micrographs (240X) of prepreg from Table 3 (condition #6): (a) center of tow, (b) tow overlap region.

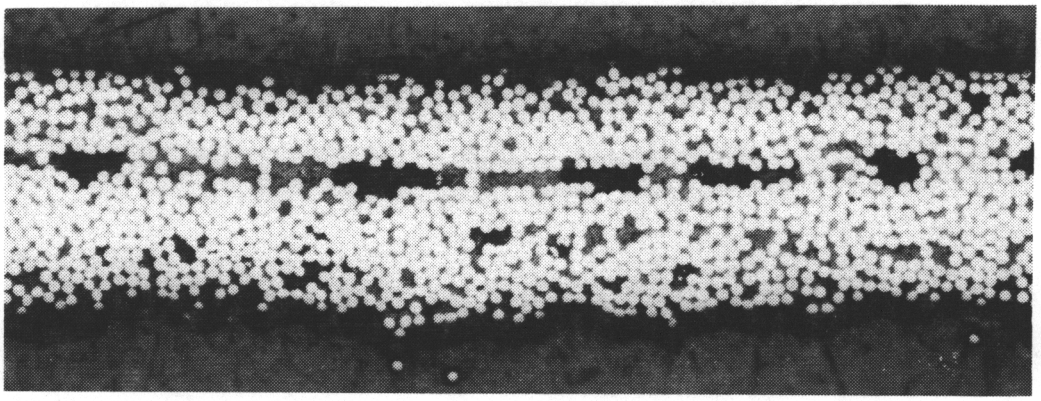


(a)

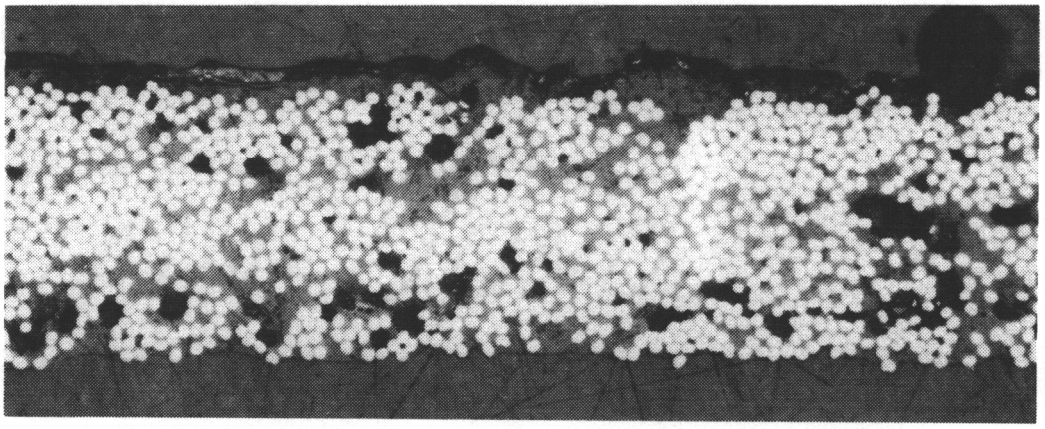


(b)

Figure 26. Micrographs of prepreg from Table 3 (200X): (a) condition #2, (b) condition #1.



(a)



(b)

Figure 27. Commercially produced amorphous thermoplastic prepreg (240X): (a) with AS4 fibers, (b) with T-300 fibers.

Both are amorphous thermoplastic/carbon fiber prepregs. The prepreg shown in (a) contains AS4 fibers, and the prepreg shown in (b) contains T-300 fibers. A commercially available semicrystalline/AS4 fiber prepreg is shown in Figure 28. This prepreg was the best observed. There is complete impregnation and a homogenous fiber distribution.

Micrographs of the double cantilivered beam (DCB) test laminate are shown in Figure 29. This laminate was manufactured from the prepreg shown in Figure 25. The resin rich regions observed are caused by the resin rich surface of the prepreg. Figure 30 (a) shows a laminate made from the prepreg shown in Figure 27 (a). Figure 30 (b) pictures a laminate made from the prepreg of Figure 28. The spots in 30 (b) are thought to be voids due to incomplete consolidation. The fiber distribution in this laminate is good.

An attempt was made to eliminate the fiber compaction by using a 40 weight percent polymer solution at slightly elevated temperatures (38°C). The resulting prepreg is shown in Figure 31. The resin rich surface was still present.

The flattening pins and guide roller are designed to keep the tow flat until it reaches the drum. The flattening pins tend to scrape the solution off of the impregnated tow, after which it drips onto the drum. A better design for the prepregger might be to remove the flattening pins and guide roller, and place the resin pot as close to the drum as possible.

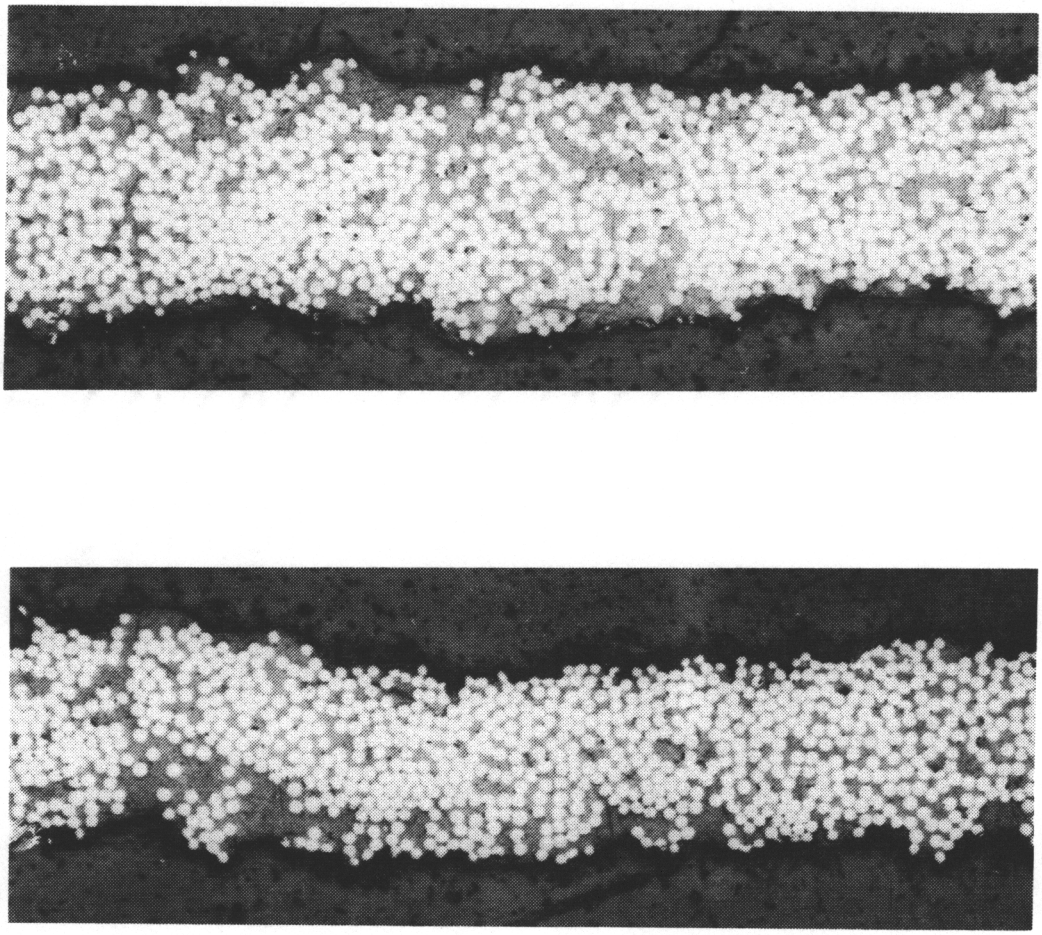
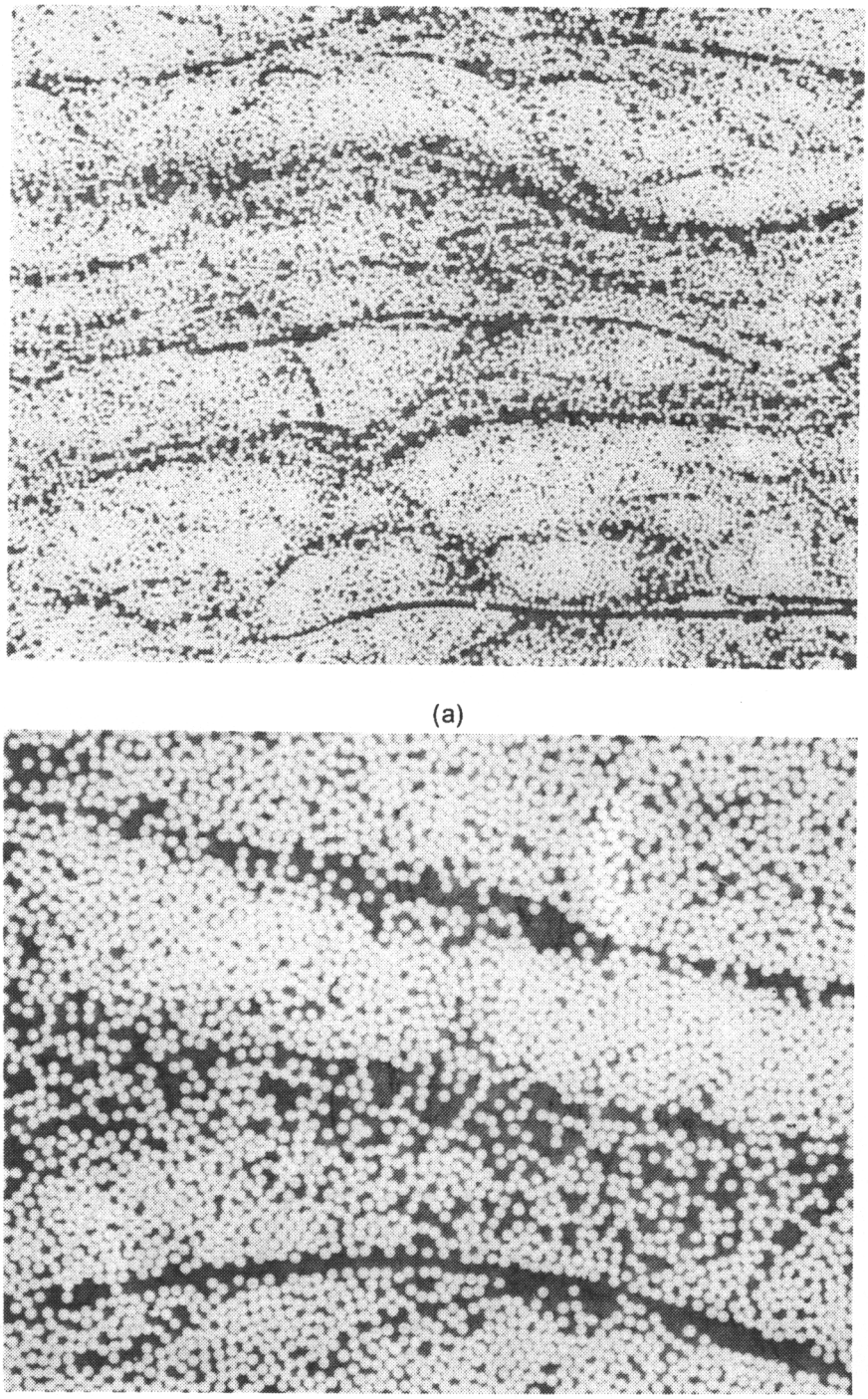


Figure 28. Commercially produced semicrystalline thermoplastic/AS4 prepreg (240X).



(a)

(b)

Figure 29. Laminate manufactured from Virginia Tech PES/AU4 prepreg: (a) 120X, (b) 240X.

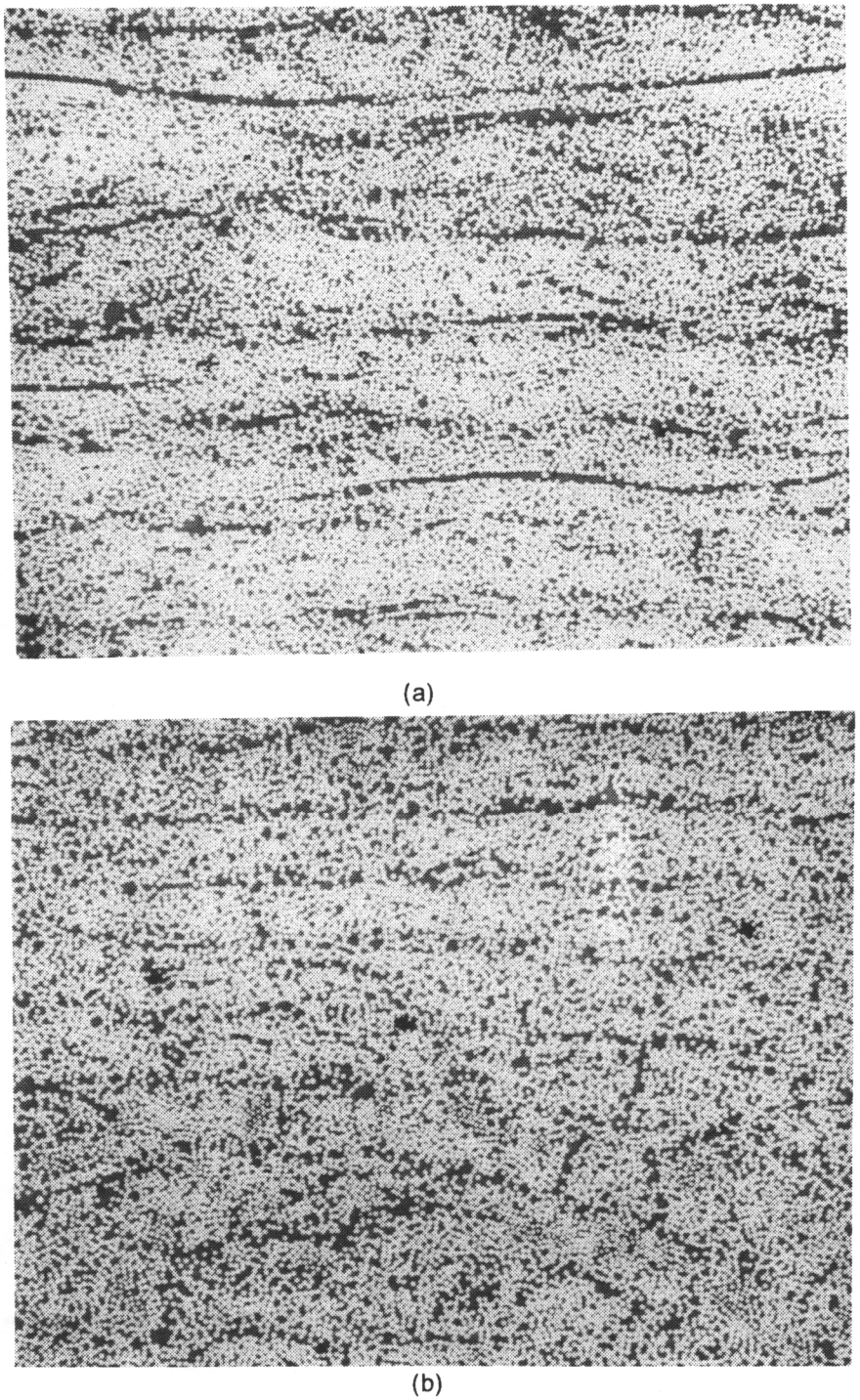


Figure 30. Laminate manufactured from commercially produced (120X): (a) amorphous thermoplastic prepreg, (b) semicrystalline thermoplastic prepreg.

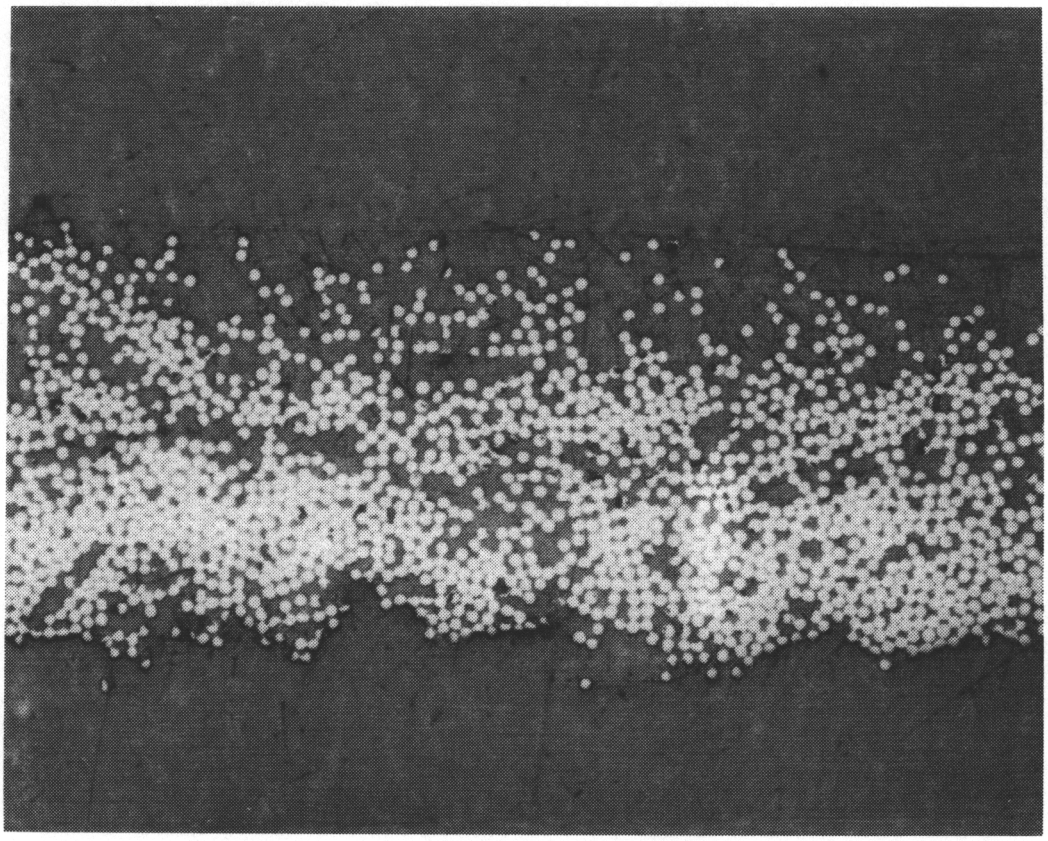


Figure 31. Prepreg produced from 40 weight percent solution (200X).

6.6 Resin Content Calculations

The assumptions from the resin content calculations discussed in Section 4.0 were, complete impregnation, and the impregnated tow cross-sectional area being equivalent to the die opening area. The best impregnation achieved was condition #6 from Table 3. From Figure 25 (a) in Section 6.5, it was obvious that the complete impregnation assumption was satisfied. The measured resin content for this prepreg was 37.1 weight percent resin. The calculated resin content was 46.9 weight percent resin. One possible source for this error could be in the second assumption. The tow is assumed to exit the die as shown in Figure 32 (a). It was thought that the tow might be necking down after exiting the die as shown in Figure 32 (b), due to the surface tension of the solution.

An experiment was performed to determine if tow necking was causing the inaccuracy. A towpreg was manufactured using the parameters of condition #6 of Table 3. When the tow was wrapped onto the drum, it was not overlapped. The towpreg was dried in the oven, and a cross-sectional micrograph was taken to assure complete impregnation (Figure 33). A resin content test was performed on three 127 cm strips of towpreg. Once the resin content was determined, the cross-sectional area of the tow, including the solvent, was calculated using simple equations. This area can be compared to the die cross-sectional area to determine if tow necking is indeed occurring. The variables used in the equations are defined in Chapter 4. Some additional terms are: F_y which is fiber yield (g/cm of fiber tow), L_t which is the length of the tow in the resin content test, and A which is the cross-sectional area of the impregnated tow. The equations used to calculate the tow cross-sectional area are shown below:

$$v_{sn} = A L_t - \frac{F_y L_t}{\rho_f} \tag{6.2}$$

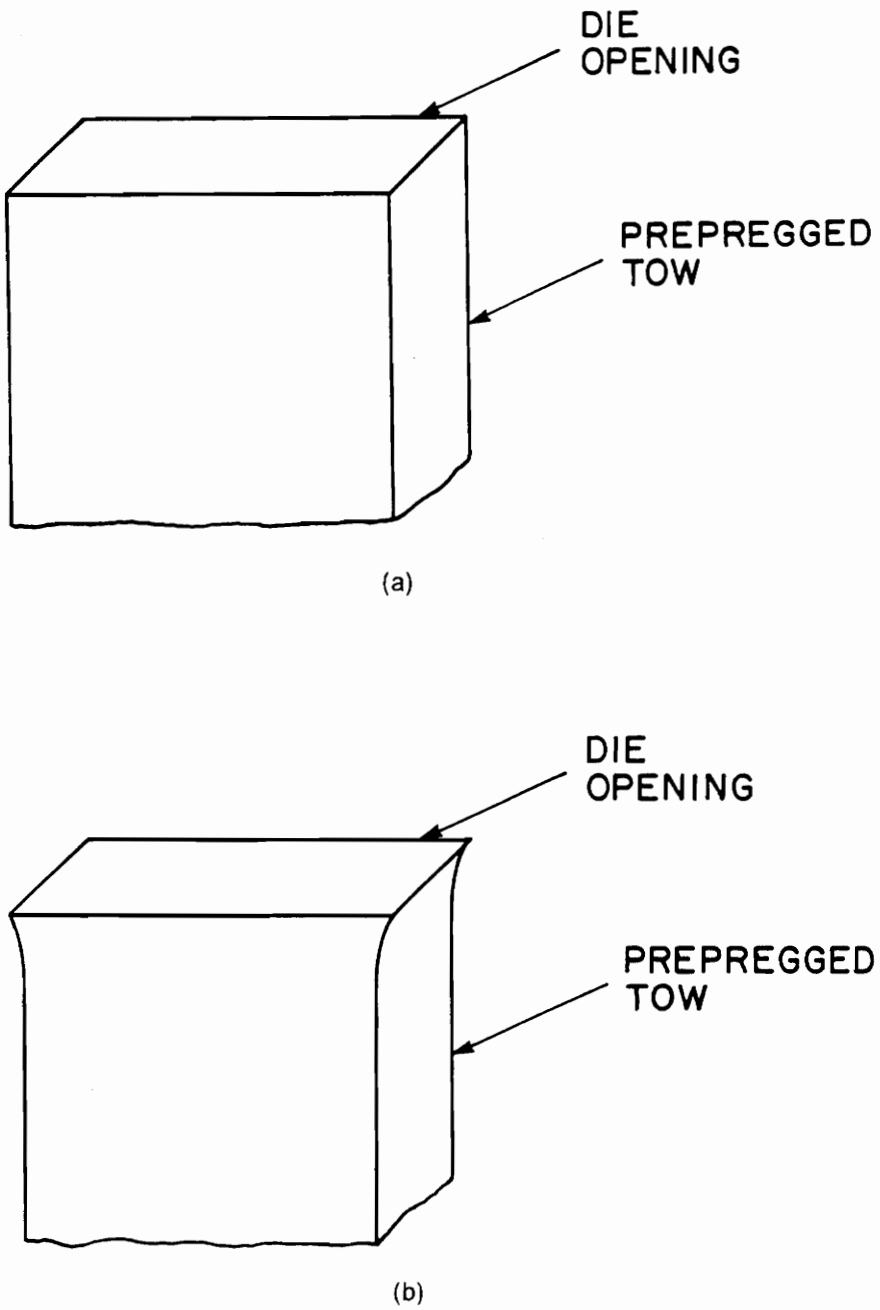


Figure 32. Tow exiting the die: (a) as assumed, (b) with necking.

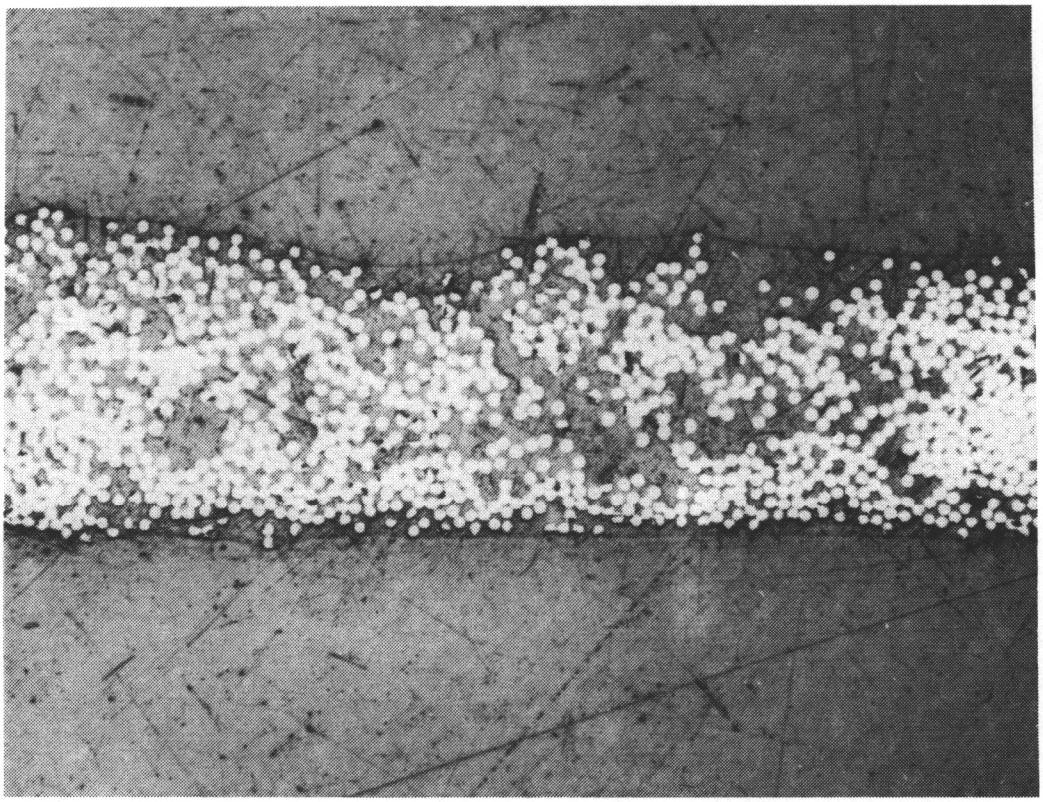


Figure 33. Cross-sectional micrograph of towpreg (240X).

$$v_{sn} = \frac{m_p}{\rho_p} + \frac{m_{st}}{\rho_{st}} \tag{6.3}$$

$$R_{sc} = \frac{m_p}{m_p + m_{st}} \tag{6.4}$$

$$m_{st} = \frac{m_p}{R_{sc}} - m_p \tag{6.5}$$

Combining 6.3 and 6.5

$$v_{sn} = m_p \left[\frac{1}{\rho_p} + \frac{1}{R_{sc}\,\rho_{st}} - \frac{1}{\rho_{st}} \right] \tag{6.6}$$

Equating 6.2 and 6.6, and solving for A:

$$A = \frac{m_p \left[\frac{1}{\rho_p} + \frac{1}{R_{sc}\,\rho_{st}} - \frac{1}{\rho_{st}} \right] + \frac{F_y\,L_t}{\rho_f}}{L_t} \tag{6.7}$$

The cross-sectional area calculated using these equations was 71% of the actual die cross-sectional area. Once the corrected cross-sectional area was used in the resin content program, there was good correlation between the measured resin content and the calculated resin content.

6.7 Mechanical Testing

6.7.1 Transverse Tensile Testing

Transverse tensile tests were performed on laminates manufactured from ICI PES/AS4 prepreg, and Virginia Tech PES/AU4 prepreg. The transverse tensile strength of the Virginia Tech laminate was expected to be lower because the fiber surface was not treated or sized. The AS4 fibers used by ICI were treated (electrolytic etch) and unsized. Several studies have been performed to determine the effects of fiber sizing and treatment on the mechanical response of composites [27, 28, 29], and these studies show that the sizing and treatment can have a significant effect on the mechanical properties. A sample stress/strain plot from the transverse tensile tests is shown in Figure 34. The transverse tensile strength and transverse modulus for each specimen is shown in Table 4. The average strain to failure of the ICI specimens was $7{,}008 \times 10^{-6}$ m/m. The average strain to failure of the Virginia Tech specimens was $5{,}346 \times 10^{-6}$ m/m. The average transverse tensile strength for the Virginia Tech laminate is 66% of the ICI laminate. The only differences in the laminates were:

- the ICI prepreg was impregnated without solvents
- the ICI prepreg was manufactured with treated AS4 fibers
- the resin content of the ICI prepreg was lower (ICI 31.0 weight percent polymer, VT 37.1 weight percent polymer)
- there was some fiber damage in the Virginia Tech prepregging process

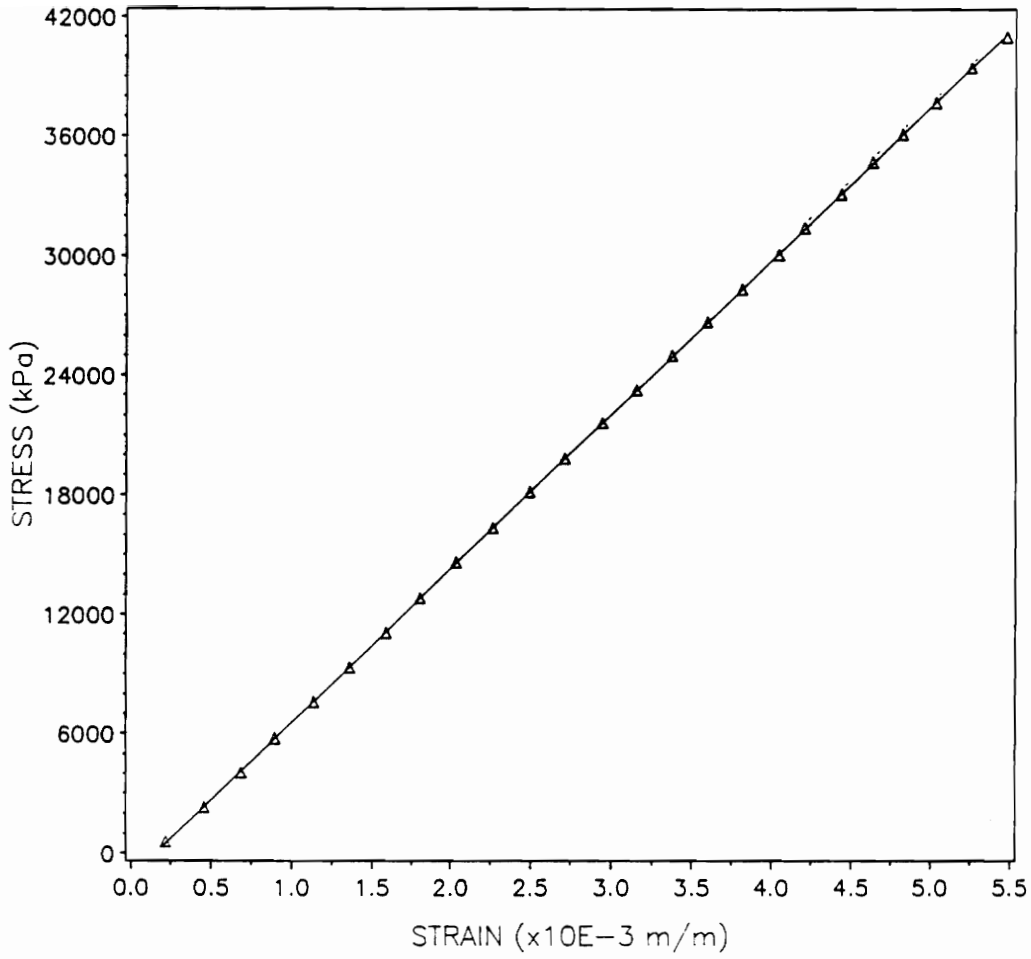
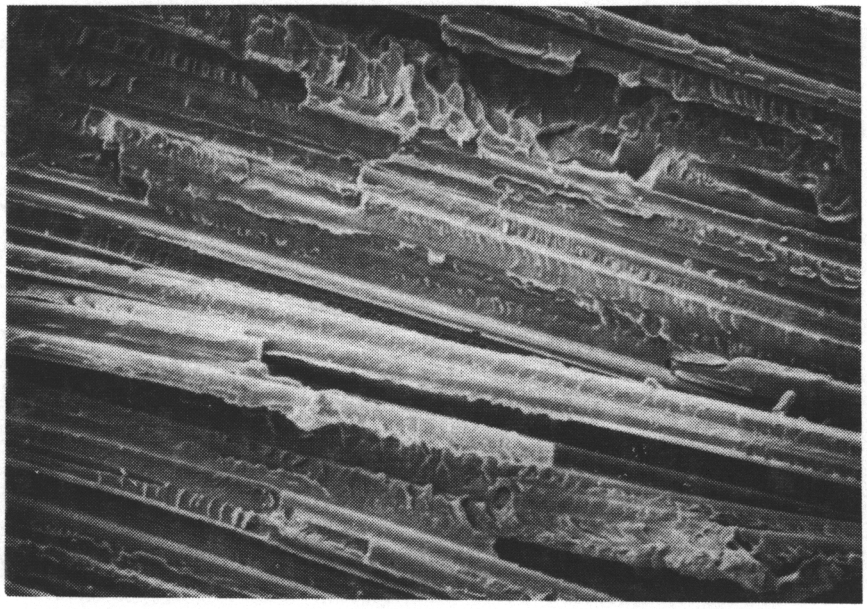


Figure 34. Typical stress/strain curve from transverse tensile tests.

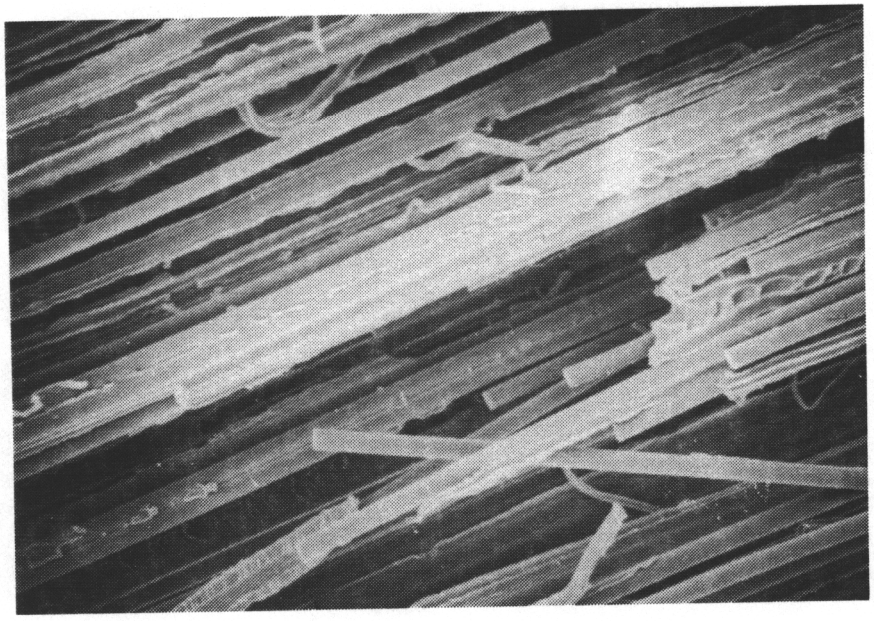
Table 4. Transverse tensile test results.

	TRANSVERSE TENSILE STRENGTH (kPa)	TRANSVERSE MODULUS (GPa)
ICI	70,126	8.956
	64,625	8.936
	56,978	8.743
	61,391	8.522
	60,908	8.977
average	62,806 (s.d. 4,911)	8.825 (s.d. 1.931)
VT	42,327	7.722
	42,113	7.660
	37,804	7.467
	41,782	7.888
	44,437	7.632
average	41,693 (s.d. 2,410)	7.674 (s.d. 0.152)

In Figure 35, fractographs are shown. From these fractographs it is obvious that the polymer adhered very well to the treated fiber surface in the ICI specimen (a), and the untreated fiber surface of the Virginia Tech specimen (b), is clean.



(a)



(b)

Figure 35. Fractographs (350X) from transverse tensile tests: (a) ICI, (b) Virginia Tech.

6.7.2 Double Cantilivered Beam Tests

The double cantilivered beam tests were performed on a laminate manufactured from the Virginia Tech PES/AU4 prepreg. Fiber bridging was present in the tests. A sample load/displacement plot is shown in Figure 36. Note from the figure that the linearity condition discussed in Section 5.10.3 is valid even for the last crack jump. All compliance/crack length data were used to calculate a third order compliance/crack length polynomial. The data, and the polynomial curve are shown in Figure 37. The critical strain energy release rate (G_{IC}) plotted with respect to crack length is shown in Figure 38. The average G_{IC} is 1010.0 kJ/m^2. The double cantilivered beam G_{IC} value for ICI manufactured PES/AU4 is 1490.0 kJ/m^2 [30]. The differences between the laminates tested by ICI and the Virginia Tech laminate were:

- the ICI prepreg was impregnated without solvents
- the resin content of the ICI prepreg was slightly lower
- there was some fiber damage in the Virginia Tech prepregging process
- ICI samples were thicker (24 plies)
- the grade of PES used by ICI was slightly different (higher molecular weight)

The Virginia Tech G_{IC} is 68% of the ICI, which is similar to the percentage difference between the ICI and the VT in the transverse tensile tests. One factor which may be causing the difference in mechanical response is the molecular weight distribution near the fiber in the solution impregnated prepreg. The solution permits the low molecular weight species to migrate to the fiber surface through increased polymer mobility [15]. This low molecular weight interphase may have an effect on the mechanical properties of the laminates. A fractograph

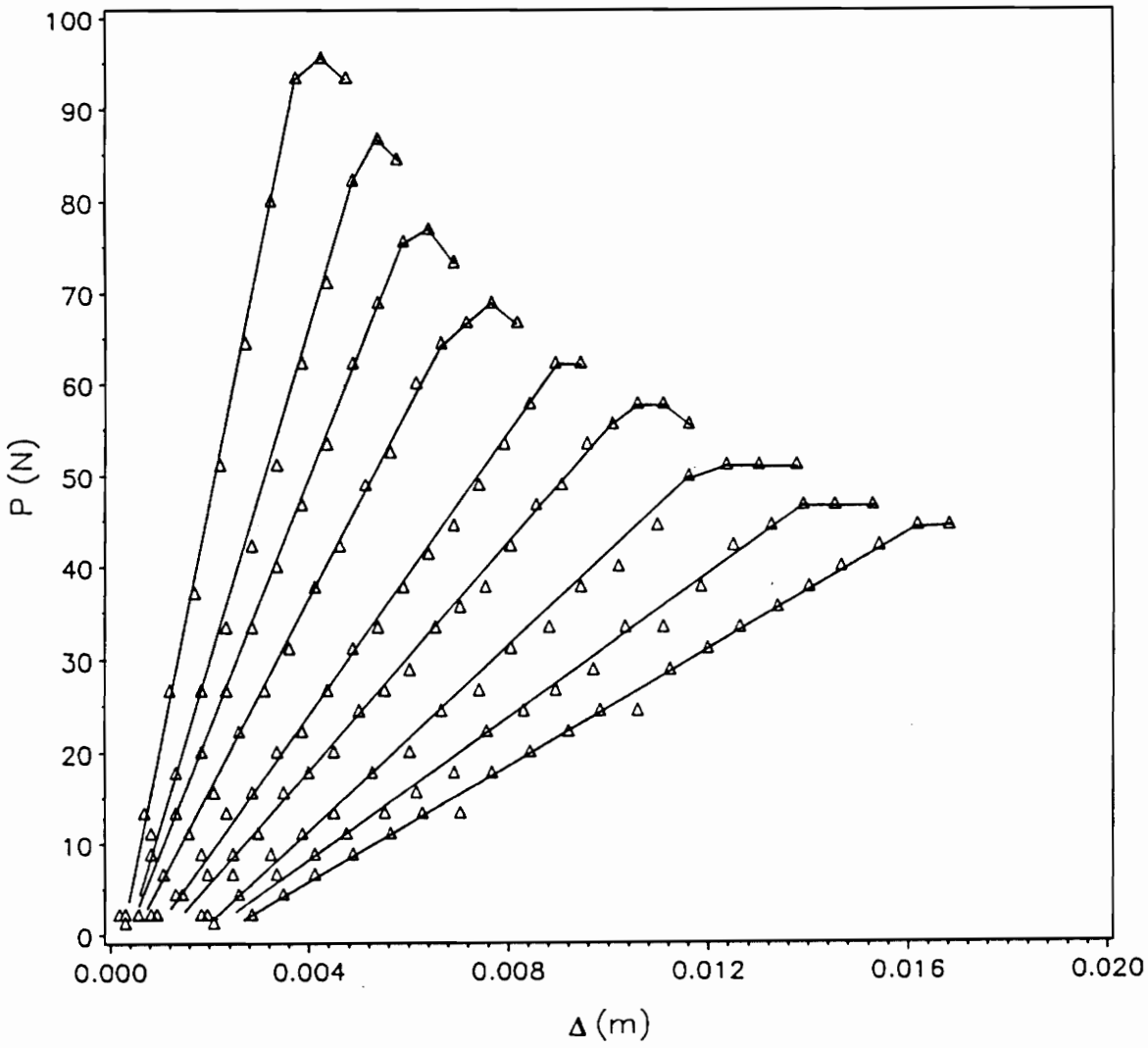


Figure 36. Double cantilivered beam load/displacement plot.

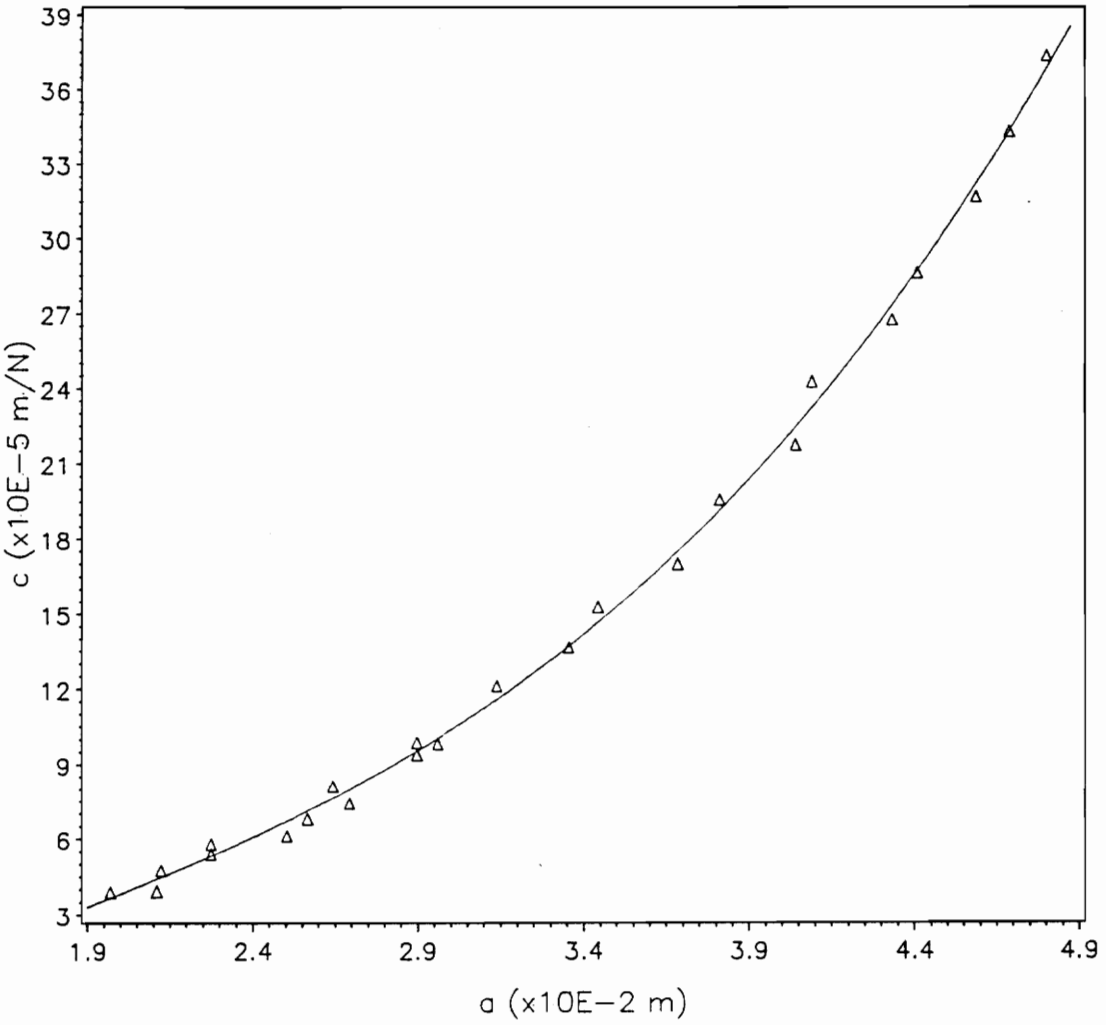


Figure 37. Double cantilivered beam master compliance/crack length curve.

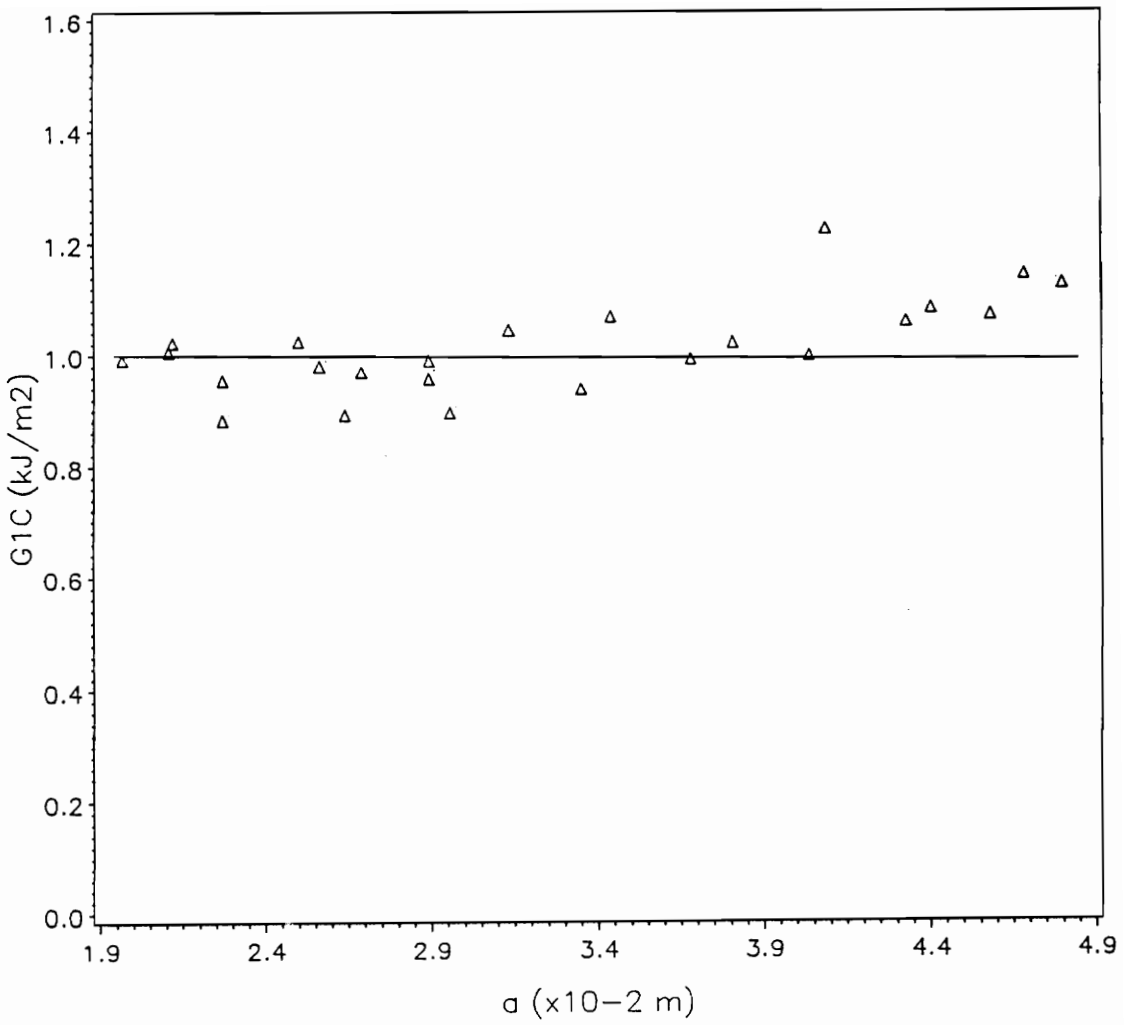


Figure 38. Double cantilivered beam critical strain energy release rate/crack length plot.

of the DCB specimen made from Virginia Tech prepreg is shown in Figure 39. The clean fiber surface is similar to what was observed in the transverse tensile test.

6.8 X-Ray Spectroscopy

The purpose of the x-ray spectroscopy was to analyze the fracture surface for any residual solvent in the laminate. The wide angle scan of the DCB fracture surface is shown in Figure 40. Each peak in the scan corresponds to an element on the specimen surface. A complete set of scans for one sample are shown in the Appendix. Scans were run on the DCB fracture surface, the PES polymer powder, and the AU4 fiber. The results from these tests are shown in Table 5. The nitrogen on the carbon fiber comes from the polyacrylonitrile (PAN) precursor fiber. The oxygen on the fiber comes from oxidation during processing. The exact chemical proportions of each repeating unit of PES polymer are:

- 75% carbon
- 18.75% oxygen
- 6.25% sulfur

Therefore from Table 5, the XPS data is within 0.19% of the actual values. In order to calculate the contribution of the polymer and the fiber to the contents of the fracture surface, the percentage area of each, on the fracture surface must be known. Since there is no sulfur on the fiber, all of the sulfur on the fracture surface is from the polymer. Hence the percentage of the surface which is PES is:

$$(3.00/6.21)100 = 48.3\%$$

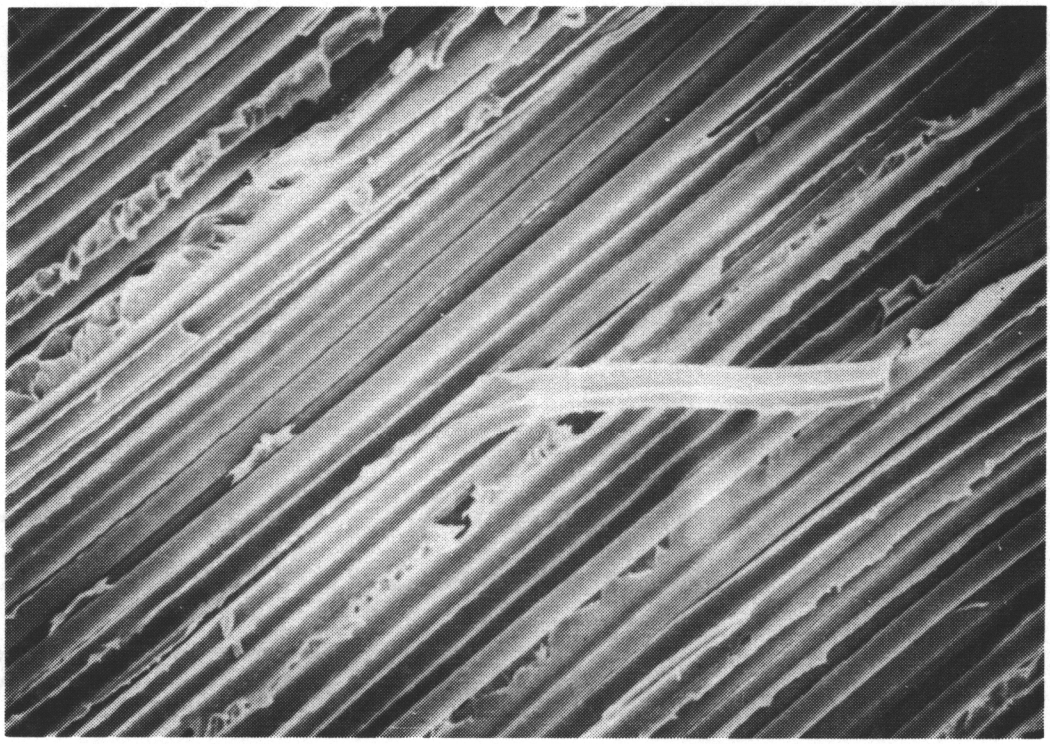


Figure 39. Double cantilivered beam specimen fractograph (410X).

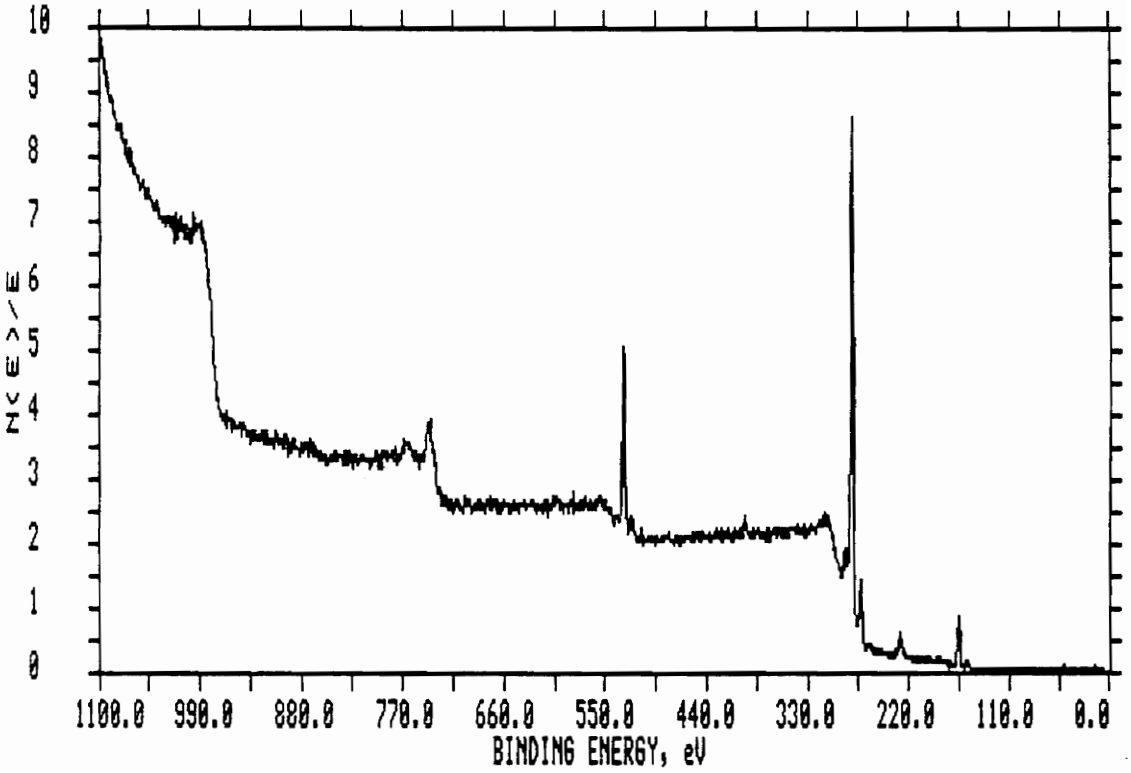


Figure 40. X-Ray photoelectron spectroscopy wide angle scan.

Table 5. X-Ray photoelectron spectroscopy results.

	CARBON (%)	OXYGEN (%)	NITROGEN (%)	SULFUR (%)
FIBER	96.39	1.52	2.10	0.00
PES	75.19	18.59	0.00	6.21
DCB	84.10	11.51	1.39	3.00

In Table 6, the first row is the second row of Table 5 multiplied by 0.483, or the calculated contribution of PES to the fracture surface composition. Similarly the second row of Table 6 is the calculated contribution of the fiber. The third row is the total calculated contribution of both the fiber and the PES. The last row shows the difference between the calculated contributions and the measured values from the specimen. The results are inconclusive because the observed residual solvent is too small to be significant and may be due to experimental error of the X-ray photoelectron spectroscopy equipment.

Table 6. X-Ray photoelectron spectroscopy calculated results.

	CARBON (%)	OXYGEN (%)	NITROGEN (%)	SULFUR (%)
PES (x 0.483)	36.32	8.98	0.00	3.00
FIBER (x 0.517)	49.82	0.79	1.09	0.00
PES + FIBER	86.14	9.77	1.09	3.00
DCB	84.10	11.51	1.39	3.00
DCB - PES	-2.04	+1.74	+0.30	0.00

7.0 Summary of Results

This work consisted of the evaluation of prepregging parameters and their effect on the integrity of the prepreg. High quality prepreg was manufactured and the prepreg was consolidated into laminates for mechanical testing.

A 30 weight percent solution of amorphous thermoplastic PES polymer in NMP solvent was found to give the best impregnation results. The viscosity of this solution at room temperature was 4.0 Pa-s. Thermogravimetric analyses were performed and it was found that the solvent was vaporized from the solution and the prepreg in 40 to 60 minutes using a temperature cycle consisting of a ramp to 300°C at 7°C/minute, followed by an isotherm.

Preliminary prepregging experiments were performed using AS4-W-12K fibers. The best prepreg was obtained using a 30 weight percent polymer solution, and prepregging at room temperature. Low fiber tow tension and the use of impregnation pins yielded the best results, although the evaluation was qualitative. In subsequent prepregging experiments, AU4-12K fibers were used. High tow velocity, high tow tension and the use of impregnation pins all resulted in improved impregnation of the fiber tow. The improvement due to high tow velocity was attributed to increased pressure within the wedge-slit die. The enhanced impregnation due to the high tow tension was thought to be caused by capillarity and wicking of the solution into the fiber tow. The high tow tension brought the fibers in the tow closer together, thus

increasing the driving force for wicking. The increased impregnation due to the impregnation pins was thought to be due to increased pressure between the pins and the fiber tow as the tow passed over the pins, the flattening and spreading of the tow over the impregnation pins, or a combination of the two. The use of the impregnation pins did cause some fiber breakage.

Calculations were performed to predict the weight percent polymer on the prepreg after solvent removal. The calculations were based on the assumptions that there was complete impregnation and that the impregnated tow was the same size as the die opening when it exited the resin pot. The resin content values obtained from the calculations were much higher than the experimentally measured values. It was thought that the tow might be necking due to the surface tension of the polymer solution. An experiment was performed, and the tow necking phenomenon was verified. When 71% of the die opening area was used in the calculations, there was good correlation between the measured and the calculated values.

Transverse tensile and double cantilivered beam testing was performed. The transverse tensile tests were performed on ICI PES/AS4 prepreg, and Virginia Tech PES/AU4 prepreg. The AS4 fibers in the ICI PES/AS4 prepreg were treated and unsized. The AU4 fibers were untreated and unsized. The transverse tensile strength of the ICI specimens was 62,806 kPa, and the Virginia Tech specimens was 41,693 kPa. Hence the transverse tensile strength of the Virginia Tech specimens was 66% of the ICI specimens. The differences were that the ICI prepreg was impregnated without solvents, the resin content of the ICI prepreg was lower, the fibers used in the ICI prepreg were treated, and there was some fiber damage in the VT prepreg.

The double cantilivered beam testing resulted in a critical strain energy release rate of $1010 kJ/m^2$ for the Virginia Tech PES/AU4 prepreg. Values for the critical strain energy release rate of ICI manufactured PES/AU4 were quoted as 1490 kJ/m^2 [30]. The G_{IC} of the Virginia Tech specimens were 68% of the ICI specimens. The differences in the prepreg were that the ICI prepreg was impregnated without solvents, and the resin content of the ICI prepreg was slightly lower, the grade of PES used by ICI was different, the ICI specimens were thicker, and there was some fiber damage in the VT prepreg.

X-ray photoelectron spectroscopy was utilized to search for residual solvent on the fracture surface of the test specimens. No significant amount of the solvent was found.

8.0 Conclusions

- Viscosities of thermoplastic solutions were characterized and a viscosity of 4.0 Pa-s was found to give best impregnation

- Solvent vaporization from solution and prepreg was characterized, most of the solvent vaporizes in the first 40 to 60 minutes of a 7° C/minute ramp to 300°C followed by an isotherm

- Increased tow velocity, increased tow tension, and the use of impregnation pins enhance impregnation

- Computer program was developed to predict resin content of prepreg prior to impregnation, corrected area was found to be 71% of die opening area, due to tow necking

- Laminates made from Virginia Tech PES/AU4 prepreg gave transverse tensile strength 66% of laminates made from ICI PES/AS4 prepreg

- Laminates made from Virginia Tech PES/AU4 prepreg yielded G_{IC} values 68% of values reported for ICI PES/AU4 prepreg

- X-Ray spectroscopy studies did not show any significant amount of solvent remaining in the laminates

9.0 Future Work

The following areas of interest are suggested for future work:

1. Increase the radius of the pins on the impregnation bar to minimize fiber damage

2. Make prepreg with treated AS4 fibers and 31 weight percent polymer, perform transverse tensile tests and compare values to ICI transverse tensile strength to quantify the loss of strength due to solvent impregnation

3. Investigate fiber surface energetics and their effect on the impregnation of the fiber tow

4. Investigate the use of polymer suspensions rather than polymer solutions in prepregging

5. Develop a flow model for the wedge-slit die geometry which accounts for surface energetics between the fiber tow and the polymer solution

6. Investigate powder prepregging

Bibliography

[1] Rogers, C. W., "Structural Design with Composites," **Fundamental Aspects of Fiber Reinforced Plastic Composites**, Ed. R. T. and H. S. Schwartz, International Scientific Publishers, New York, 1966, p. 141.

[2] Lubin, George, **Handbook of Fiberglass and Advanced Plastics Composites**, Robert E. Krieger Publishing Company, New York, 1975, p. 421.

[3] Breukers, J. J., Woo, E. M., Seferis, J. C., "Experimental Evaluation of the Prepregging Process," **Proceedings of the Third Technical Conference**, American Society for Composites, Seattle, Washington, September, 1988, pp. 12-22.

[4] Lee, W. J., Seferis, J. C., "Prepreg Processing Science," **SAMPE Quarterly**, Vol. 17, No. 2, January 1986, PP. 58-68.

[5] Molyneux, M., "Prepreg, Tape and Fabric Technology for Advanced Composites," **Composites**, Vol. 14, No. 2, April, 1983, pp. 87- 91.

[6] Custer, M. F., Vicknair, K. E., "Pultrusion Impregnated Thermoplastic Tape," **Proceedings of the Third Technical Conference**, American Society for Composites, Seattle, Washington, September, 1988, pp. 293-297.

[7] Muzzy, J., Varughese, B., Thammongkol, V., Tincher, W., "Electrostatic Prepregging of Thermoplastic Matrices," **Proceedings of the 34th International SAMPE Symposium**, May 8-11, 1989, pp. 1940-1951.

[8] Edie, D. D., Gantt, B. W., Lickfield, G. C., Drews, M. J., Ellison, M. S., "Thermoplastic Coating of Carbon Fibers," **Advances in Thermoplastic Matrix Composite Materials, ASTM STP 1044**, G. M. Newaz, Ed., American Society for Testing and Materials, Philadelphia, 1989, pp. 50-61.

[9] Sendeckyj, G. P., personal communication, WRDC/FIBEC WPAFB 45433-6553, Flight Dynamics Lab, (513)255-6104.

[10] Welhart, E., K., "How to Fabricate Advanced Composites," **Materials Engineering**, August, 1977, pp. 50-53.

[11] Newaz, G. M., "Advanced Thermoplastic Composites," **ASTM Standardization News**, Vol. 15, No. 2 October, 1987, pp. 32-35.

[12] Leeser, D., Banister, B., "Amorphous Thermoplastic Matrix Composites for New Applications," Presented at the 21st International SAMPE Technical Conference, Atlantic City, New Jersey, September, 1989.

[13] Clemans, S., Hartness, T., "Thermoplastic Prepreg Technology for High Performance Composites," **SAMPE Quarterly**, July 1989, pp. 38-42.

[14] Nelson, K. M., Seferis, J. C., Zachmann, H. G., "Determination of Solvent Induced Crystallization in Polyetherimide Matrix Composites by Wide Angle X-Ray Scattering," **Proceedings of the 34th International SAMPE Symposium**, May 8-11, 1989, pp. 69-78.

[15] Pangelinan, A. B., McCullough, R. L., Kelley, M. J., "Polymer Molecular Weight Distributions near Surfaces and Their Effects on Thermoplastic Composite Properties," presented at the AIChE Annual Symposium, San Francisco, California, November, 1989.

[16] Fitzer, E., Hannes, G., Jager, H., "Fabrication of Carbon Fibre Reinforced Thermoplastics Polycarbonate and Polysulfone," **Proceedings of the Nonmetallic Materials and Composites at Low Temperatures Conference**, Heidelberg, West Germany, August, 1984, pp. 161-166.

[17] Mettenet, M., personal communication, Hercules Aerospace Company, Composite Products Group, Bacchus Works, Magna, Utah, 84044-0098, (801)251-5376.

[18] Underwood, G., personal communication, Hercules Aerospace Company, Composite Products Group, Bacchus Works, Magna, Utah, 84044-0098, (801)251-5383.

[19] Wilkins, D. J., Eisenmann, J. R., Camin, R. A., Margolis, W. S., Benson, R. A., "Characterizing Delamination Growth in Graphite-Epoxy," **Damage in Composite Materials, ASTM STP 775**, K. L. Reifsnider, Editor, American Society for Testing and Materials, 1982, pp. 168-183.

[20] Keary, P. E., Ilcewicz, L. B., Shaar, C., Trostle, J., "Mode I Interlaminar Fracture Toughness of Composites Using Slender Double Cantilivered Beam Specimens," **Journal of Composite Materials**, Vol. 19, March, 1985, pp. 154-176.

[21] Leach, D. C., Curtis, D. C., Tamblin, D. R., "Delamination Behavior of Carbon Fiber/Poly(etheretherketone) (PEEK) Composites," **Toughened Composites, ASTM STP 937**, Norman J. Johnston, Editor, American Society for Testing and Materials, Philadelphia,
1987, pp. 358-380.

[22] Carlsson, L. A., Pipes, R. B., **Experimental Characterization of Advanced Composite Materials**, Prentice Hall Inc., Englewood Cliffs, N.J., 1987, p. 163.

[23] Pedersen, L. C., "A Study of the Characteristics of Wetting on Carbon Fibers by a Change in Polymer Concentration," Senior Project, July, 1989, Department of Chemistry, VPI&SU, Blacksburg, VA, 24061.

[24] Chmielewski, C., Jayaraman, K., Petty, C. A., "An Experimental and Theoretical Study of Resin Impregnation Rates into Fiber Bundles Using a Wedge Slit Die," presented at the Third Technical Conference of The American Society for Composites, Seattle, Washington, 1988.

[25] Batchelor, G. K., **An Introduction to Fluid Dynamics**, Cambridge University Press, New York, 1967.

[26] Tzeng, J. T., Loos, A. C., "A Model of the Winding and Curing Processes for Filament Wound Composites," CCMS-89-01, October 1988, Department of Engineering Science and Mechanics, VPI&SU, Blacksburg, VA 24061.

[27] Wilkinson, S., "Preparation of Composite Materials at Fiberite During Summer 88", Internal ICI Report, September 1988.

[28] Drzal. L. T., Rich, M. J., Subramoney, S., "The Interdependence Between Fiber-Matrix Adhesion and Composite Properties," **Proceedings of the Third Technical Conference**, American Society for Composites, September, 1988, Seattle, Washington.

[29] Briggs, D., Hearn, M. J., Hodge, D. J., Middlemiss, B., Peacock, J. A., "Correlation Between Fibre Surface Energetics and Fibre-Matrix Adhesion in Carbon Fibre Reinforced PEEK Composite," Presented at the Materials Research Society Symposium, Tailored Interfaces in Composites, Boston, December, 1989.

[30] Leeser, D., personal communication, December 1988, ICI, 2055 East Technology Circle, Tempe, Arizona, 85284, (602)730-2010.

Appendix

Resin Content Calculation Program and Output

```
      IMPLICIT REAL*8(A-H,O-Z)
C     ********************************************************************************
C     **************
C     INPUT SECTION
C     **************
C
      PRINT *,'PES / NMP / AU4'

C
      A=0.5588
C     A IS THE WIDTH OF THE DIE (CM)
C
      B=0.0508
C     B IS THE SLIT OF THE DIE (CM)
C
      RSC=0.2888
C     RSC IS THE RESIN SOLIDS CONTENT OF THE SOLUTION
C     (WEIGHT PERCENT RESIN)
C
      FY=0.0085531
C     FY IS THE FIBER YIELD (GRAMS/CM)
C
      RP=1.37
C     RP IS THE DENSITY OF THE POLYMER (GRAMS/CUBIC CENTIMETER)
C
      RF=1.774
C     RF IS THE DENSITY OF THE FIBER (GRAMS/CUBIC CENTIMETER)
C
      RST=1.03
C     RST IS THE DENSITY OF THE SOLVENT(GRAMS/CUBIC CENTIMETER)
C
C     ***************
C     OUTPUT SECTION
C     ***************
C     VT =  THE TOTAL VOLUME OF ONE LINEAR FOOT OF PREPREGGED TOW
C           (CUBIC CENTIMETERS/LINEAR FOOT = CC/M)
C     VF =  THE VOLUME OF ONE LINEAR FOOT OF FIBER TOW (CC/M)
C     VSN = THE VOLUME OF SOLUTION IN ONE LINEAR FOOT OF PREPREGGED TOW
C           (CC/LM)
C     RSN = THE DENSITY OF THE SOLUTION (G/CC)
C     VP =  THE REQUIRED VOLUME OF POLYMER TO GET THE DESIRED VOLUME
C           PERCENT RESIN IN THE FINAL PREPREG
C           (AFTER EXTRACTING SOLVENT, CC/LM)
C     VPR = THE VOLUME PERCENT RESIN OF THE PREPREG AFTER
C           SOLVENT VAPORIZATION (% BY VOLUME)
C     WPR = CALCULATED WEIGHT PERCENT RESIN OF THE PREPREG AFTER
C           EXTRACTING THE SOLVENT(% BY WEIGHT)
C     ********************************************************************************
C     CALCULATIONS
C     ************
      VT=A*B*100.0
      VF=FY*100.0/RF
      VSN=VT-VF
      RSN=1/(RSC/RP+(1-RSC)/RST)
      VP=VSN*RSN*RSC/RP
```

```
      VPR=VP/(VP+VF)
      WPR=(VP*RP)/(VP*RP+VF*RF)
C     ************************************************************************
C     PRINTING
C     ********
      PRINT *,' '
      PRINT 10,A
   10 FORMAT (' THE WIDTH OF THE DIE (CM)              =  ',F6.4)
      PRINT 20,B
   20 FORMAT (' THE SLIT OF THE DIE (CM)               =  ',F6.4)
      PRINT 40,FY
   40 FORMAT (' THE FIBER YIELD (GRAMS/LINEAR M)       =  ',F5.3)
      PRINT 50,RP
   50 FORMAT (' THE DENSITY OF THE RESIN (GRAMS/CC)    =  ',F4.2)
      PRINT 60,RF
   60 FORMAT (' THE DENSITY OF THE FIBER (GRAMS/CC)    =  ',F4.2)
      PRINT 70,RST
   70 FORMAT (' THE DENSITY OF THE SOLVENT (GRAMS/CC) =  ',F4.2)
      PRINT 75,RSC
   75 FORMAT (' THE RESIN SOLIDS CONTENT OF THE SOLUTION (% WEIGHT) = ',
     &F4.2)
      PRINT *,' '
      PRINT *,' '
      VPRR=VPR*100.0
      PRINT 30,VPRR
   30 FORMAT (' THE VOLUME PERCENT RESIN OF THE PREPREG AFTER SOLVENT
     &VAPORIZATION          = ',F6.2)
      WPRR=WPR*100.0
      PRINT 35,WPRR
   35 FORMAT (' THE CALCULATED WEIGHT PERCENT RESIN OF THE PREPRG AFTER
     &SOLVENT VAPORIZATION = ',F6.2)
      STOP
      END
```

Output From Resin Content Calculation Program

```
PES / NMP / AU4

THE WIDTH OF THE DIE (CM)              =  0.5588
THE SLIT OF THE DIE (CM)               =  0.0508
THE FIBER YIELD (GRAMS/LINEAR M)       =  0.009
THE DENSITY OF THE RESIN (GRAMS/CC)    =  1.37
THE DENSITY OF THE FIBER (GRAMS/CC)    =  1.77
THE DENSITY OF THE SOLVENT (GRAMS/CC) =  1.03
THE RESIN SOLIDS CONTENT OF THE SOLUTION (% WEIGHT) = 0.29


THE VOLUME PERCENT RESIN OF THE PREPREG AFTER SOLVENT   VAPORIZATION         =  53.34
THE CALCULATED WEIGHT PERCENT RESIN OF THE PREPRG AFTER SOLVENT VAPORIZATION =  46.89
```

X-Ray Photoelectron Spectroscopy Output

Tabulated Results

Ion Gun:OFF X-ray: ON Mg Neutralizer:OFF Acquiring Technique:ESCA

0.4mPa 12/11/89 16:16

Atomic Concentration

1 Peak Measurement Use Height Area Element Name

2 Included Regions 1 2 3 4

Atomic Concentration Table

File: kg2

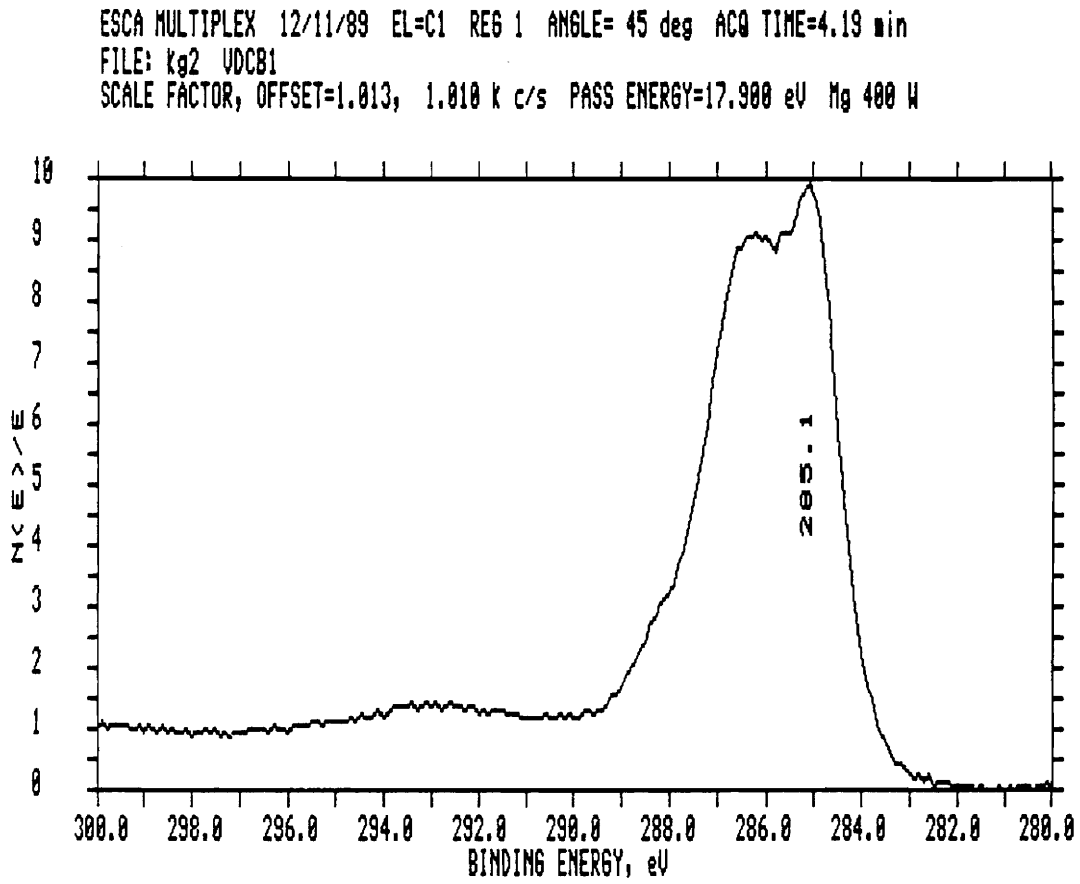
Comment: VDCB1

Input Lens: Small Area Omni Focus

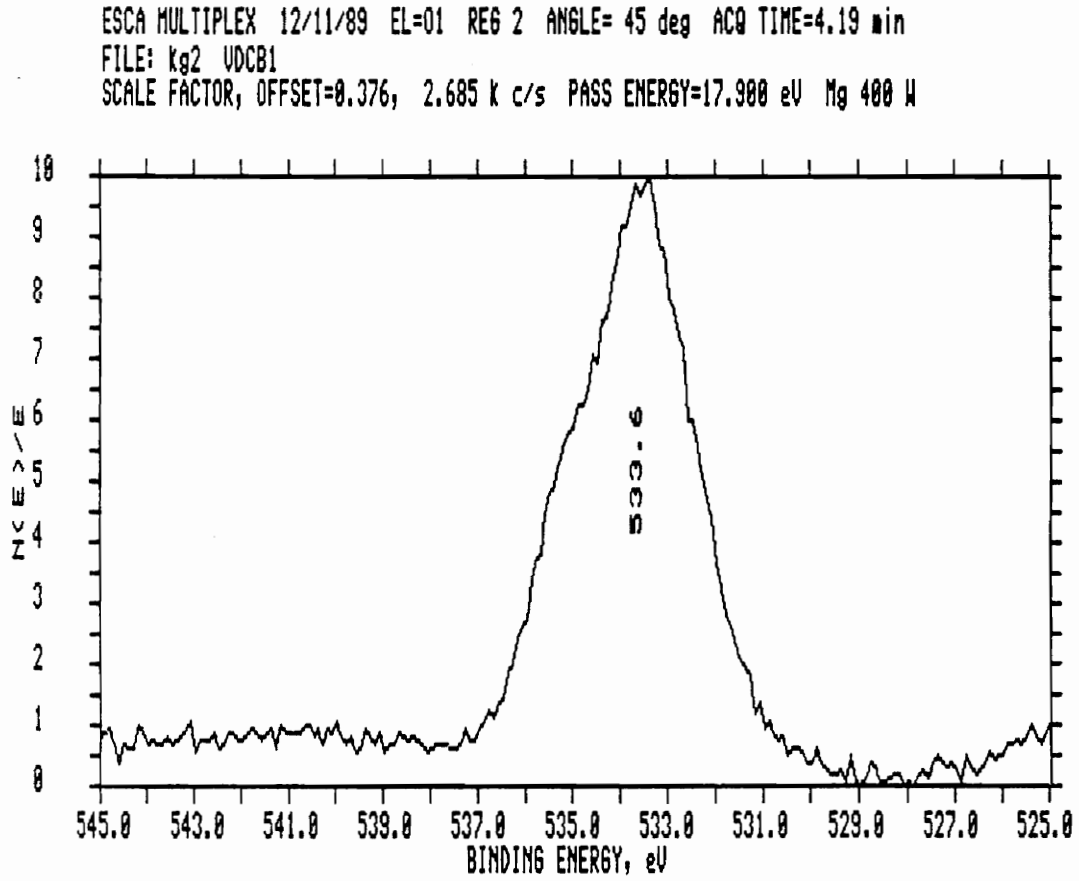
Element	Concentration(%)	Sens. Factor
C1s	84.10	0.296
O1s	11.51	0.711
N1s	1.39	0.477
S2p	3.00	0.666

AC Table AC to AC Summary Omit All Exit

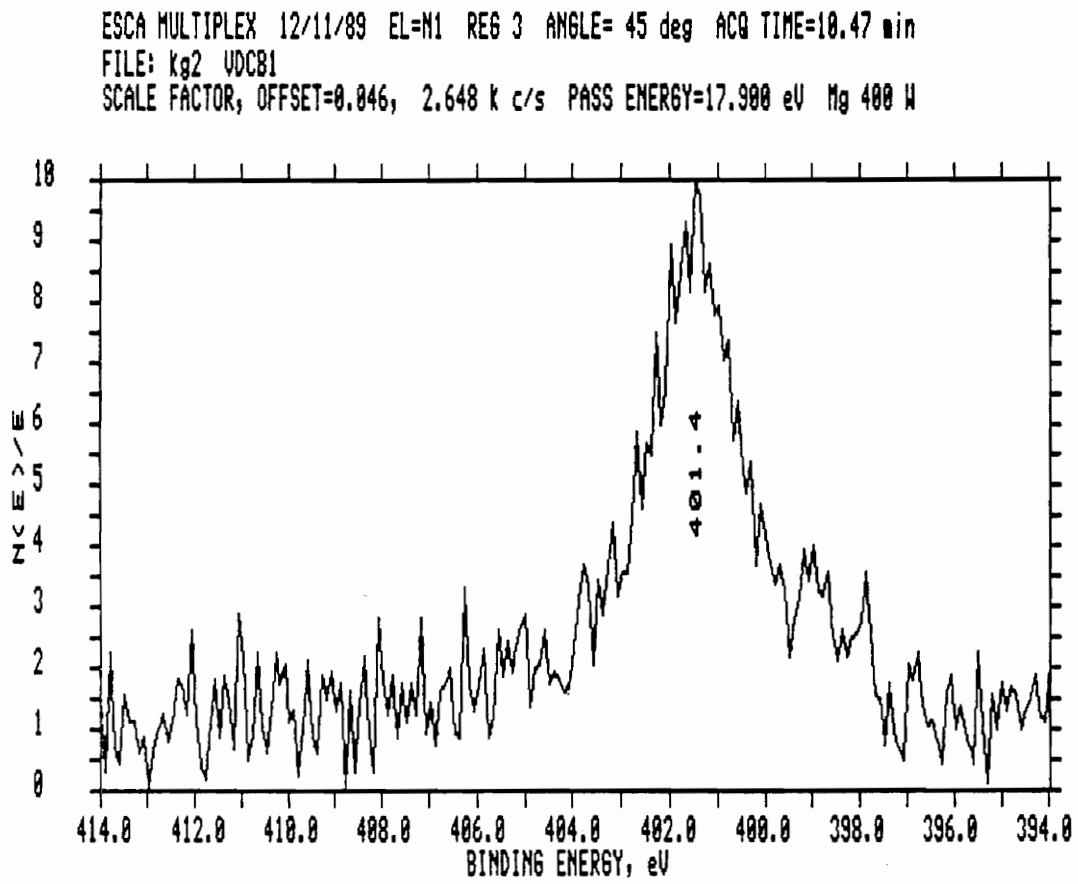
Narrow Angle Scan for Carbon



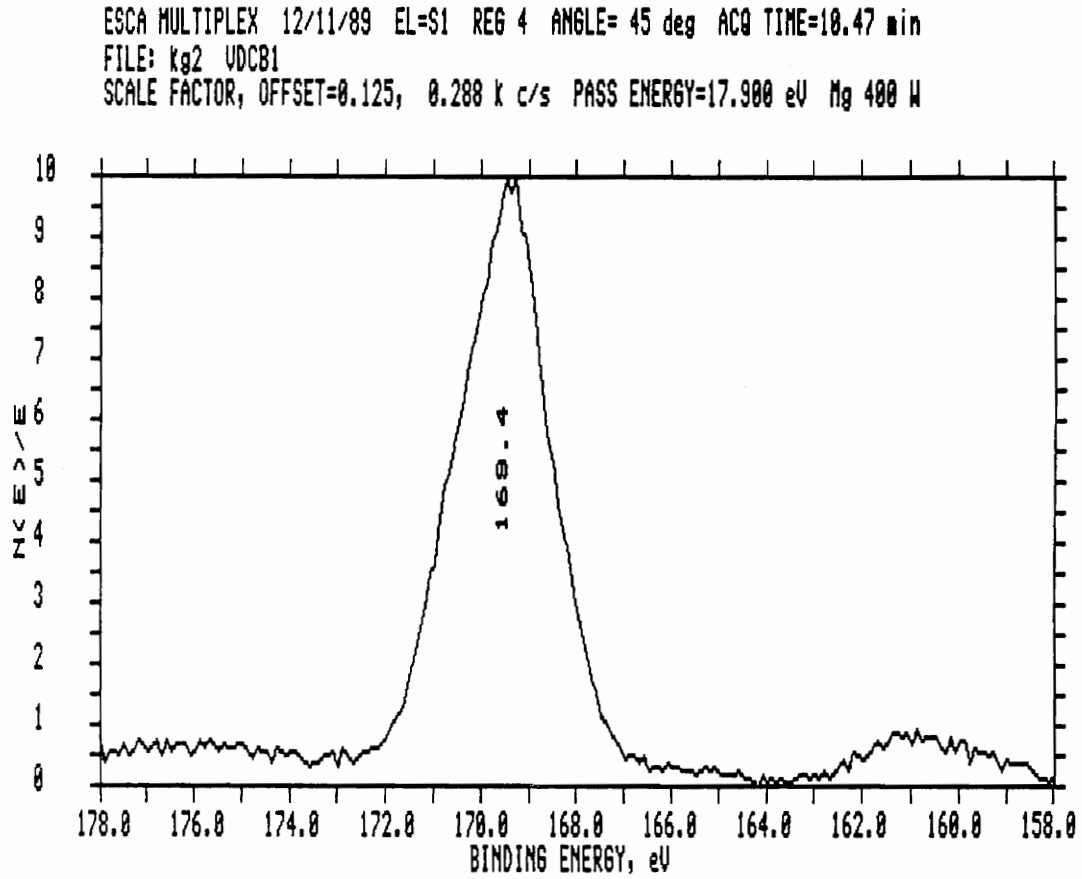
Narrow Angle Scan for Oxygen



Narrow Angle Scan for Nitrogen



Narrow Angle Scan for Sulfur



Vita

The author was born to Joseph Gillam Goodman III and Elketha Celeste Goodman on June 25, 1965, in Dallas, Texas. He attended North Mesquite High School and graduated in Spring of 1983. In the Fall of 1983 he began studies at The University of Texas at Arlington in the Mechanical Engineering Department. While at UTA, he participated in the London Semester program in the Spring of 1987. He graduated with a Bachelors Degree in Mechanical Engineering in May of 1988. He began studies towards a Masters Degree in the Engineering Mechanics Department at Virginia Polytechnic Institute and State University in August of 1988. After completing the requirements for a Masters Degree at Virginia Tech, the author will be employed by General Dynamics, Fort Worth Division.